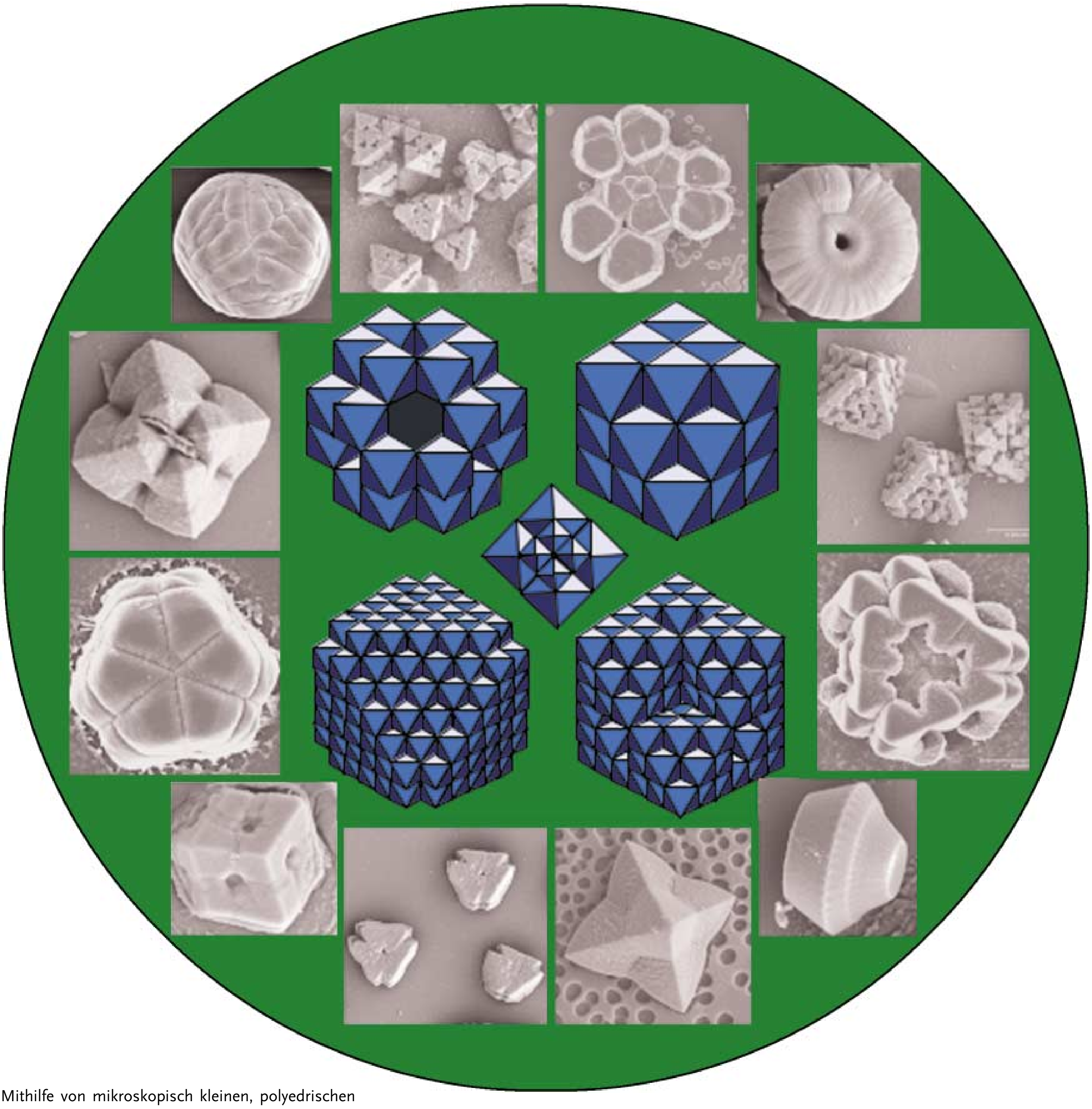
Zuschriften



Mithilfe von mikroskopisch kleinen, polyedrischen selbstorganisierten Kristallen als Bausteinen bilden sich spontan große Kristalle und offene Mesophasen, in denen Form und Orientierung der zugrundeliegenden Struktureinheiten bewahrt bleiben. Diese Strukturen stehen in Einklang mit einfachen geometrischen Modellen. Mehr zu diesem Thema erfahren Sie im Beitrag von Liu et al. auf den folgenden Seiten.

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Self-Assembly with Crystals

Hierarchical and Self-Similar Growth of Self-Assembled Crystals**

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Biomaterials, such as seashells[1,2] and diatoms[3] display rich morphologies and multiple-scale ordering. Recently remarkable biomaterial-like morphologies were reported in synthetic, self-assembled mesophase silicates.[4–8] The formation of these unusual shapes is related to curvature effects and is independent of the basic structural units.[4,5] Hierarchical mesoporous oxides and patterned films were prepared by combining micropatterning with surfactant self-assembly.[9–13] In addition, ordered patterns and open structures were assembled from millimeter-sized objects.[14–16] Synthetic materials containing biological patterns were also prepared using pre-existing templates.[17–19] Furthermore, fractal growth has been investigated in some simple crystalline systems.[20–22] Herein, we report a novel hierarchical and self-similar crystal-growth process leading to the spontaneous formation of large objects with controlled morphology and ordering from nano- to macro-scale. To our knowledge this is the first report of true hierarchical and self-similar crystal growth for self-assembled materials based on the assembly of microscopic polyhedral single crystals.

Self-assembled periodic silicates were first reported in 1992 from silicic acid and quaternary ammonium surfactants.[23,24] Since then hybrid silanes and bridged organic silsesquioxanes have been used to prepare mesoporous powders[25–28] and films.[29,30] Recently Inagaki and co-workers prepared well-defined hybrid mesoporous crystals using 1,2-bis(trimethoxysilyl)ethane (BTME) as a silica source and hexadecyltrimethylammonium chloride (CTAC) as a surfactant.[31] Herein, we use the hybrid organic silane BTME along with CTAC to create a new class of supported hierarchical mesophase crystals (that is, large mesophase structures formed from crystalline building blocks) through heterogeneous nucleation and growth.[32] BTME and CTAC were mixed in basic aqueous solutions and heated in a Teflon container. A microscope glass slide was placed vertically in the container to allow the crystals to nucleate and grow on the surface.

Well-defined and oriented mesophase crystals were formed on the glass surface within 30 minutes. Figure 1a shows a typical scanning electron microscopy (SEM) image of large arrays of the mesophase crystals. These crystals are rather uniform in shape and size (12 μm wide). Low-angle X-ray diffraction (XRD) and transmission electron microscopy (TEM) indicate that these mesophase crystals have a cubic structure ($Pm3n$, $a_0 = 98$ Å) as reported in the literature.[31] Figure 1b shows a TEM image of the $<001>$ zone axis square lattice of the cubic structure. As will be discussed later, the crystals in Figure 1a are secondary octahedral structures formed from primary octahedral crystals, and are oriented with one of the {111} planes parallel to the substrate. We further demonstrated that these mesocrystals can be patterned on preformed polystyrene lines on glass substrates (Figure 1c). The formation of oriented mesophase crystals is significant for practical applications, but to date there have been few reports on how to prepare uniform and oriented self-assembled crystals. In contrast, the particles that precipitated from the solutions under similar conditions have a wide range of morphologies and have poorly defined shapes (Figure 1d).

Hierarchically ordered large crystals and open structures can be constructed through multiple and self-similar growth. Figure 2 and Figure 3 show some examples of the high-order structures and schematic representations of how they are formed. Figure 2a and 3a are the primary 5 μm octahedral crystals formed by the {111} planes of the cubic phase. Figure 2b shows a commonly observed rosette-like structure viewed from different angles, and indicate that these crystals

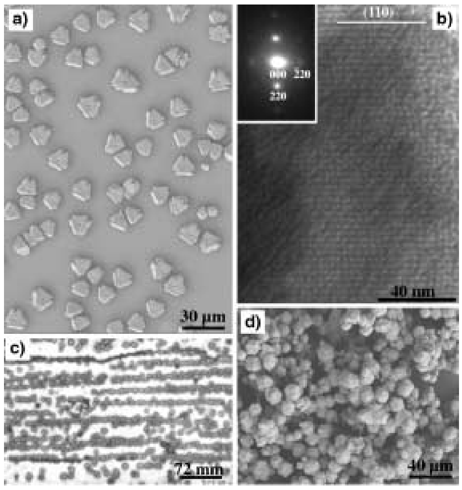

Figure 1. Oriented mesophase crystals on a glass substrate: a) large arrays of oriented mesophase crystals. One of the {111} planes of the mesocrystals is parallel to the glass surface, b) TEM image of the square lattice in the $<001>$ orientation, c) aligned mesophase crystals on patterned glass surface, d) heterogeneous particles precipitated from the solution.

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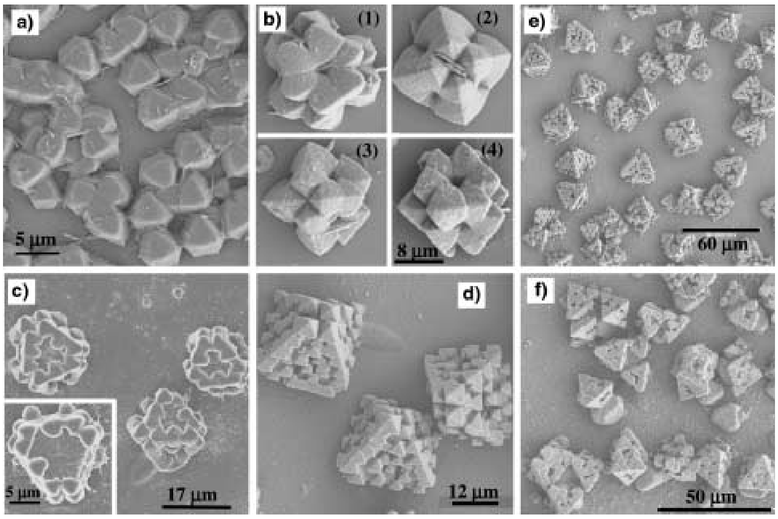

Figure 2. Hierarchically ordered octahedral open crystal structures: a) primary octahedral crystals, b) secondary octahedral crystals: 1) face-on, 2) top view from one corner, 3) edge-on, 4) tilted edge-on, c) tertiary octahedral crystals. The insert shows small octahedral units nucleated on a secondary rosette crystal, d) large open octahedral objects containing five primary octahedral units on each side, e) large area view of high-order open structures, f) large open structures assembled from tertiary units.

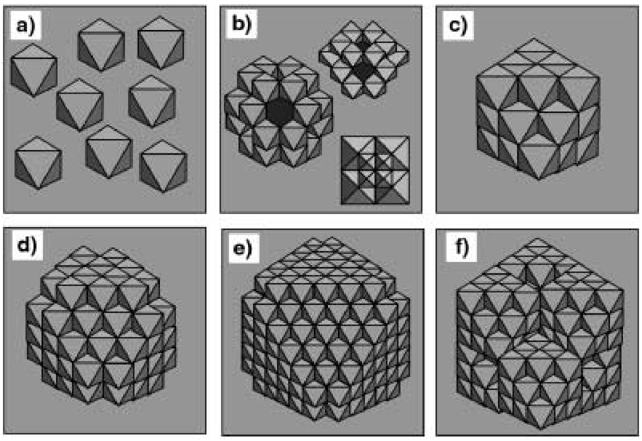

Figure 3. Schematic illustrations of edge-sharing stacking: a) primary octahedral units, face-on configurations, b) quartet-octahedron model for the secondary structure, c) tertiary structure with filled corners, d) tertiary structure with unfilled corners, e) a high-order structure from primary octahedra, f) a high-order structure from tertiary units.

are secondary structures made of primary octahedral subunits shown in Figure 2a. The secondary structure is about 11 µm in width, two times the size of the primary structure, and is based on a quartet-octahedron model with 24 edge-sharing octahedral primary subunits (Figure 3b). The model contains four surfaces made of six subunits and six corners made of four subunits. This model differs from the real crystal slightly in that the real crystal appears denser (no large voids at the center) than the model, which is not surprising because the open structure would have a tendency to grow to a higher density. The mesophase crystals can also become truncated by the substrate on certain orientations. For example, the face-on rosette (Figure 2b(1)) can be reproduced by truncating the quartet-octahedron model in the middle plane and by allowing the octahedral units to deform to permit denser packing. Similarly, the end-on (top) configuration (Figure 2b(2)) can be derived if only one third of the quartet-octahedron structure (8 units) is allowed to grow and the quartet on the bottom is allowed to grow to a larger size.

On a large length scale, high-order structures can be derived by edge-sharing growth. These large mesophase crystals are remarkable in several ways. First, these structures are not close-packed and contain large empty spaces (cages), but they still have almost perfect octahedral shapes. Second, the octahedral subunits in the large structure are all about 5 µm in size and are fairly uniform. These subunits are also well aligned throughout the crystal by edge sharing. Finally, the high-order octahedral mesophase crystals are also rather uniform in size. Figure 2c and Figure 3d show the tertiary octahedral structures containing three subunits on each side. The width of the tertiary structure is 16 µm, roughly three times the size of the primary crystal. Figure 2d (high magnification), 2e, and Figure 3e illustrate even higher order structures about 25 µm in width, which contain five units on each side. Furthermore, large open octahedral structures are not only formed from primary octahedral units, but can be also derived from secondary and tertiary structures. Figure 2f and Figure 3f show a high-order structure consisting of filled tertiary octahedral units (Figure 3c) that still preserve the overall octahedral shape.

Currently the detailed growth mechanism is still under investigation, but there is strong evidence that the large structures are formed through step-wise nucleation from the edges of previous crystals. The insert in Figure 2c is an incomplete tertiary structure, clearly showing new octahedral crystals formed on the edge of secondary crystals. Here, one side of the secondary structure is yet not covered with new crystals.

By systematically varying the experimental conditions, such as the temperature, surfactant concentration, and reaction time, a wide range of morphologies were observed based on polyhedral crystal stacking. Among these crystals (Figure 4) are triangular rosettes, round rosettes, flowerlike patterns, stars, cubelike cages, large rhombic dodecahedral structures.[33] Although the morphologies shown in Figure 4 appear to be complex, they are based on similar cubic crystal stacking and can be controlled. For example, a higher temperature and a higher surfactant concentration favor the formation of better defined, and more facetted crystals. Figures 4a and 4b are high magnification images of Figure 1a. These secondary crystals were formed after 3 h as compare to 30 minutes for the rosette crystals in Figure 2b. The crystals are almost octahedral in shape, but the individual octahedral units are no longer obvious. However, the tips of the individual octahedral units can still be observed when the crystals are tilted and it is possible to envision how these

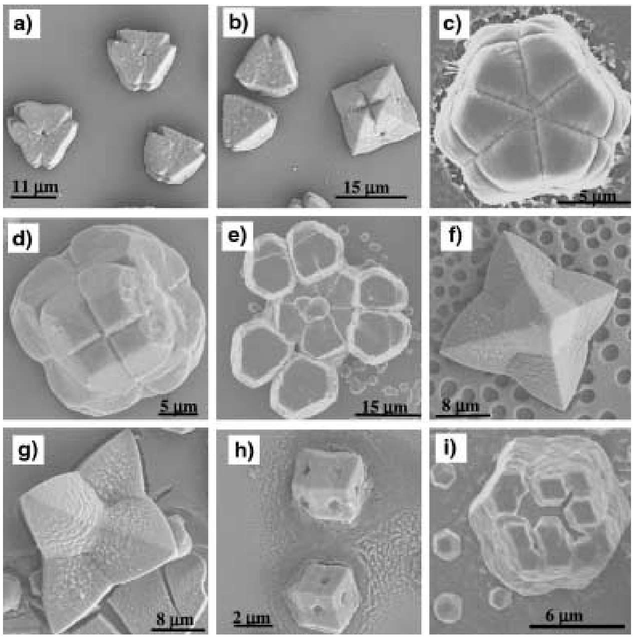

Figure 4. Various morphologies of mesophase crystals formed on glass surfaces through polyhedral stacking: a) triangular rosettes, b) tilted triangular rosettes, c) rounded rosettes, d) tilted rounded rosettes, e) flowerlike patterns, f) stars, g) tilted stars, h) cubelike cages by face-sharing growth, i) large rhombic dodecahedra by face-sharing growth.

crystals can be derived from the quartet-octahedron. Similarly, the morphologies in Figure 4c and Figure 4d share the same origin as the quartet model, except here some surfaces of the octahedral subunits are truncated. The flowerlike pattern in Figure 4e is formed by growing truncated octahedral crystals on the tips of the octahedral subunits in the rosette.

We have also shown that different mesophase crystals can be formed through different stacking patterns, and grown with different orientations. For example, the starlike particles shown in Figure 4f and 4g are derived from six edge-sharing octahedral units with some deformation of the primary crystals. The cubelike cages and the large rhombic dodecahedron in Figure 4h and Figure 4i are formed through face-on stacking of different kinds of subunits. The formation of different crystal shapes with different orientations will be the subject of future publications.

In conclusion, we have demonstrated true multiscale hierarchical structures through self-similar assembly of polyhedral mesophase crystals. This work shows that complex structures and morphologies can be derived from the fundamental microscopic building units, and the final morphologies are correlated with the structure and shape of the basic crystal. Octahedral edge-sharing stacking is commonly observed in true atomic crystals,[34] but extensive and continuous 3D open structures through edge sharing as reported herein are rare. The unusual hierarchical structures and the complex morphologies may shed new light on self-assembly and crystal growth. These results also point to how one can start with basic structural units to design and build large hierarchical structures with controlled size, orientation, and morphology. This approach can be adapted for large-scale preparation on patterned substrates. In nature, hierarchical ordering is critical for the functional needs of biomaterials. Synthetic materials containing biomimetic patterns mostly involve using a pre-existing patterns and template.[14–19] Some of the morphologies observed show similarities with those from diatoms, and therefore may lead to new thinking on how these biominerals are formed. The ability to spontaneously form such ordered hierarchical structures could lead to novel applications of self-assembled materials.

Experimental Section

A typical molar ratio for BTME:CTAC:NaOH:H_2O is 1:x:2.36:353, where x (the concentration of the surfactant) was varied from 0.45 to 1.70. After BTME, CTAC , NaOH, and H_2O were mixed together, the resulting solutions were stirred and aged overnight. Only solutions that became clear after aging were used for our experiments. The aged solution was transferred to a Teflon container. A microscope glass slide (or tin oxide coated glass slide) was placed vertically in the Teflon container. The reaction temperature ranged from room temperature to 115°C. High-order crystals, such as shown in Figures 2c to 2f were formed by repeated growth under the same conditions.

The XRD results were obtained on a Scintag PADV diffractometer at the University of New Mexico, with six peaks at 69, 48, 45, 40, 31, and 25 Å assigned to the 110, 200, 210, 211, 310, and 400 reflections of the *Pm*3*n* structure ($a_o = 98$ Å). The TEM image was obtained on a JEOL 2010 high-resolution microscope at 200 keV.

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Metalloprotein Conformation

Sliding Helix and Change of Coordination Geometry in a Model Di-Mn^{II} Protein**

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In metalloenzymes, the protein matrix tunes the dynamic and structural properties of their metal ion cofactors to catalyze a wide range of reactions with remarkable catalytic efficiencies.[1] As the reaction proceeds, the metal ions must cycle between different ligation and sometimes also oxidation states;[2] the protein plays an active role in stabilizing and catalyzing the interconversion of these intermediates.[3–5] Shifts of key carboxylate side chains and other localized motions are often observed in response to changes in oxidation state and the binding of exogenous ligands.[6–8] The de novo design of novel artificial proteins that have predictable structures and functions is the most challenging goal in protein design and mimicry. Creating functional artificial metalloproteins requires a detailed understanding of the protein-folding mechanism as well as of the coordination chemistry of the metal centers. Herein we demonstrate a sliding-helix mechanism for stabilizing a change in the ligand environment of DF1, a model di-Mn^{II} protein.

Recently, we designed DF1 as a highly simplified model for diiron/dimanganese proteins.[9] This class of protein includes a number of functionally diverse structures including diiron proteins such as the radical-forming R2 subunit of ribonucleotide reductase[10] and methane monooxygenase,[11] as well as dimanganese proteins[12] such as catalase[13] and arginase.[14] DF1 is a dimer of helix-loop-helix motifs with a dimetal site near the center of the four-helix-bundle structure. As in natural diiron proteins, two Glu side chains bridge both metal ions, while the other two carboxylates interact with a

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