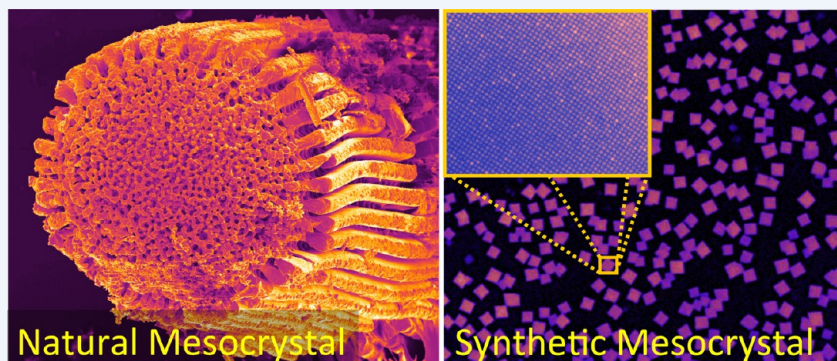


Mesocrystals in Biominerals and Colloidal Arrays

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CONSPECTUS: Mesocrystals, which originally was a term to designate superstructures of nanocrystals with a common crystallographic orientation, have now evolved to a materials concept. The discovery that many biominerals are mesocrystals generated a large research interest, and it was suggested that mesocrystals result in better mechanical performance and optical properties compared to single crystalline structures. Mesocrystalline biominerals are mainly found in spines or shells, which have to be mechanically optimized for protection or as a load-bearing skeleton. Important examples include red coral and sea urchin spine as well as bones. Mesocrystals can also be formed from purely synthetic components. Biomimetic mineralization and assembly have been used to produce mesocrystals, sometimes with complex hierarchical structures. Important examples include the fluorapatite mesocrystals with gelatin as the structural matrix, and mesocrystalline calcite spicules with impressive strength and flexibility that could be synthesized using silicatein protein fibers as template for calcium carbonate deposition. Self-assembly of nanocrystals can also result in mesocrystals if the nanocrystals have a well-defined size and shape and the assembly conditions are tuned to allow the nanoparticles to align crystallographically. Mesocrystals formed by assembly of monodisperse metallic, semiconducting, and magnetic nanocrystals are a type of colloidal crystal with a well-defined structure on both the atomic and mesoscopic length scale.

Mesocrystals typically are hybrid materials between crystalline nanoparticles and interspersing amorphous organic or inorganic layers. This structure allows to combine disparate materials like hard but brittle nanocrystals with a soft and ductile amorphous material, enabling a mechanically optimized structural design as realized in the sea urchin spicule. Furthermore, mesocrystals can combine the properties of individual nanocrystals like the optical quantum size effect, surface plasmon resonance, and size dependent magnetic properties with a mesostructure and morphology tailored for specific applications. Indeed, mesocrystals composed of crystallographically aligned polyhedral or rodlike nanocrystals with anisotropic properties can be materials with strongly directional properties and novel collective emergent properties. An additional advantage of mesocrystals is that they can combine the properties of nanoparticles with a structure on the micro- or macroscale allowing for much easier handling.

In this Account, we propose that mesocrystals are defined as “a nanostructured material with a defined long-range order on the atomic scale, which can be inferred from the existence of an essentially sharp wide-angle diffraction pattern (with sharp Bragg peaks) together with clear evidence that the material consists of individual nanoparticle building units”. We will give several examples of mesocrystals and discuss the structural characteristics for biominerals, biomimetic materials, and colloidal arrays of nanocrystals. The potential of the mesocrystal materials concept in other areas will be discussed and future developments envisioned.

■ INTRODUCTION

Materials science teaches that there is no perfect crystalline material. Indeed, defects often limit the mechanical performance of ceramics, but can also be manipulated to tailor the properties of, for example, semiconductors and catalysts. The limitations of single phase materials can be overcome by tailored combinations of two or more compounds into

composites with properties that are distinctly different from the constituents. Mineralized tissues produced by living organisms are composites with outstanding properties consisting of abundant minerals and biopolymers, for example,

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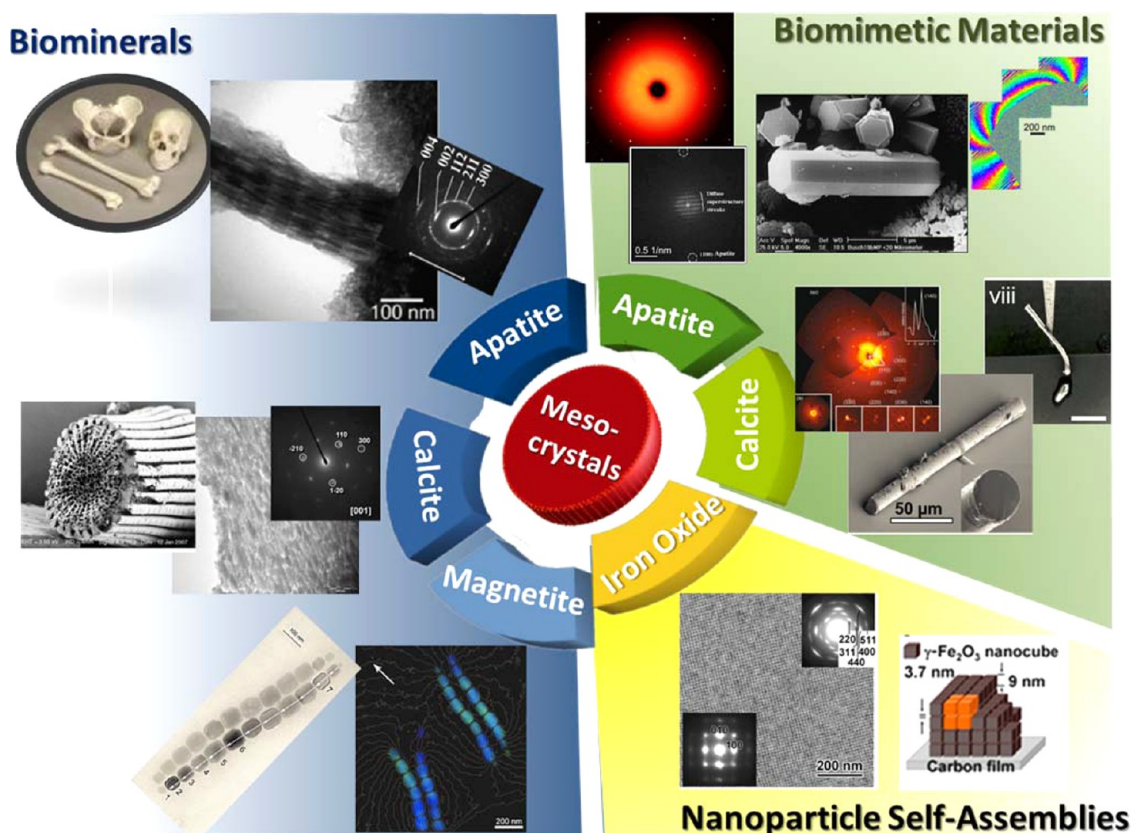


Figure 1. Schematic illustration of mesocrystals in biomaterials, biomimetic composite materials, and colloidal arrays with their structural features. The images corresponding to bone (Biomaterials, Apatite) are reprinted from ref 29 © (2007), with permission from Elsevier; sea urchin (Biomaterials, Calcite) are reprinted from Seto et al. (ref 20), National Academy of Sciences USA; magnetotactic bacteria (Biomaterials, Magnetite) are reprinted with permission from Olszta et al. (ref 29), © (2007) IOP Publishing; fluoroapatite-gelatin (Biomimetic Materials, Apatite) are reproduced from ref 30 with kind permission from Springer Science and Business Media and from ref 31 with permission from The Royal Society of Chemistry; calcite spicules (Biomimetic Materials, Calcite) are reprinted from Natalio et al. (ref 32) with permission from AAAS; maghemite nanocubes (Nanoparticle Self-Assemblies, Iron Oxide) are reprinted from Ahnizay et al. (ref 21), © (2007) National Academy of Sciences USA.

carbonates, silica and calcium phosphates in combination with proteins such as collagen and polysaccharides such as chitin. Lowenstam and Weiner^{1–3} pioneered the biomineralization research area, and we are now unraveling the design, formation, and structure of biomineral composites and realize how this knowledge can be utilized in the production of better materials—the field of biomimetics or bioinspired materials science.^{4–6}

The well-studied mollusk shell or nacre illustrates how the combination of a hard and stiff mineral (calcium carbonate) and a small amount of soft and ductile organics can yield lightweight composites with a high strength and impressive fracture toughness, about 3000 times higher than that of the mineral.⁷ The exquisite structural control, from the nanoscale and up to the cellular level and beyond, is an intrinsic feature of most biominerals that strongly relates to the impressive performance and multifunctional properties. Here, the organization of the mineral phase has attracted the most attention, and Addadi, Weiner and Mann were among the first to elucidate the control and design principles in biomineralization.^{4,8,9}

It was early recognized that organisms exert precise and exquisite control of the mineralization process, including the chemistry and location of the mineralization site, the size and shape of a specific mineral polymorph particles, as well as spatial organization in the inorganic–organic biomineral

composite. Studies on both natural armor and biological and bioinspired composites have shown that the orientation of the often highly anisotropic inorganic particles and rodlike polysaccharides into, for example, laminates, cross-ply patterns, and Bouligand structures have a strong influence on, for example, the mechanical performance.^{10–12}

Recently, detailed studies have revealed that submicrometer biomineral particles are frequently organized into superstructures of nanocrystals with common crystallographic orientation, so-called mesocrystals,^{13–17} which relate to the remarkable mechanical and optical properties.^{16,18} Mesocrystalline nanocomposites like nacre can suppress crack propagation along cleavage planes while maintaining high moduli, resulting in a remarkable combination of high fracture toughness and high strength.¹⁹ Also, mesocrystalline sea urchin spines are mechanically optimized by their hybrid design of amorphous phase and crystalline CaCO_3 .²⁰

Mesocrystals are not only produced during biomineralization. Recent work has shown that nanoparticle arrays with superstructures composed of nanocrystals with common crystallographic orientation can be produced by self-assembly.^{21–23} Assembly of colloids into colloidal crystals dates back to the seminal work on clays and proteins by Langmuir²⁴ and was later demonstrated beautifully by Pusey and van Megen in their study on the phase behavior of monodisperse polymer spheres.²⁵ With the rapid development in nanoparticle

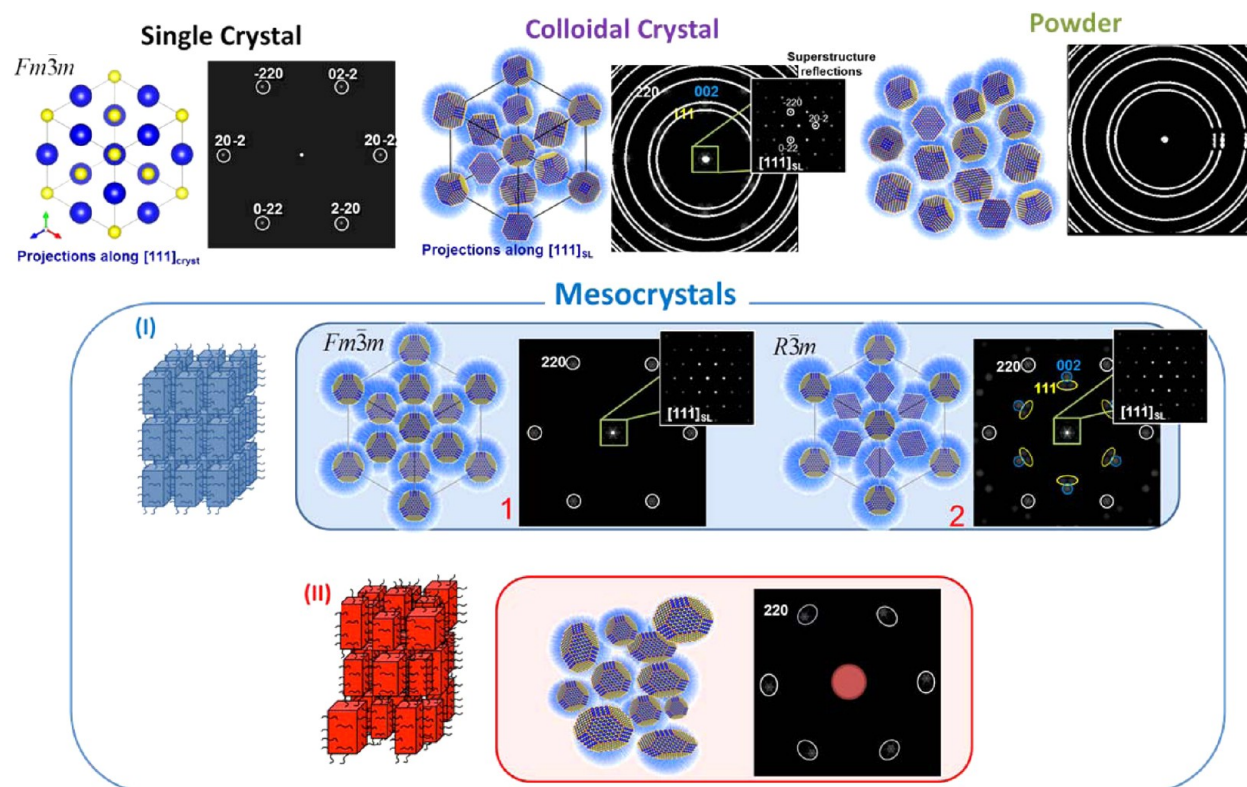


Figure 2. Schematic illustration of different types of crystalline materials with corresponding diffraction patterns. For illustrational purposes, the crystalline material (nanoparticle) has rock salt type crystal structure (S.G. $Fm\bar{3}m$) and in the case of colloidal crystals the crystalline nanoparticles are stabilized by organic molecules (blue shell) and arranged in a fcc superlattice (S.G. $Fm\bar{3}m$). (Top row) Single crystal, colloidal crystal, and powder with corresponding diffraction patterns. (Bottom row) Mesocrystals: Type I, colloidal crystals with mutually oriented monodisperse nanocrystals (characterized by single crystalline like diffraction pattern in the small angle region and single crystalline (1) or textured (2) pattern in the wide angle region); type II, colloidal aggregates with mutually oriented polydispersed nanocrystals with a possible certain degree of orientational mismatch. Figures adapted from ref 22.

synthesis originating from the seminal work by Brus et al., Bentzon et al., and others,^{26,27} we now have a plethora of nanoparticles of different compositions, shapes, and functionalities that are used as building blocks to construct nanoparticle arrays with complex structures and useful properties.²⁸ Nanoparticle arrays with both orientational and positional order, that is, self-assembled mesocrystals, have the potential to combine the properties of the anisotropic nanocrystalline building blocks with the collective properties of the interacting nanoparticles in the mesocrystal.

In this Account, we attempt to highlight the strong similarity of the structural features of mesocrystals in biominerals and colloidal arrays without discussing formation mechanisms as summarized in Figure 1. Starting with a definition of the mesocrystal concept, we will give examples of mesocrystals in biominerals, biomimetic composite materials, and colloidal arrays, illustrate the structural features, and relate that to their mechanical, optical, and magnetic properties.

■ WHAT ARE MESOCRYSTALS?

Mesocrystals were first coined about 10 years ago¹³ to define and name mesoscopically structured crystalline materials. As the field has developed and more examples of mesocrystals in both biominerals and synthetic materials have been identified, mesocrystals are defined as superstructures consisting of nanocrystals with common crystallographic orientation, either perfectly or only slightly misaligned with respect to each other.^{14,15,30,33,34} Hence, while mesocrystals can diffract X-rays

and electrons similar to a single crystal, they consist of mesoscopic (submicrometer) crystalline building blocks and thus display distinct structural features on at least two different length scales: the nanoparticles must be crystalline, and the packing arrangement of the submicrometer building blocks must allow a common crystallographic orientation. Mesocrystals can consist of both monodisperse and polydisperse crystalline nanoparticles if the material still demonstrates the specific mutual crystallographic orientation resulting in a single crystal-like or texture diffraction pattern with sharp Bragg peaks in the wide-angle region. When the mesocrystal is built up from monodisperse nanoparticles with a well-defined shape, it is possible that also the packing arrangement displays a long-range order. This type of mesocrystal, obtained, for example, through self-assembly of nanocrystals, is in essence colloidal crystals where the nanocrystals have a common crystallographic orientation. For other mesocrystals, the small-angle diffraction pattern can represent the whole range of arrangements from well-ordered to disordered (single crystalline to amorphous-like).

Building on the definition of “crystal” given by IUCr,³⁵ we propose that mesocrystals are defined as “a nanostructured material with a defined long-range order on the atomic scale, which can be inferred from the existence of an essentially sharp wide angle diffraction pattern (with sharp Bragg peaks) together with clear evidence that the material consists of individual nanoparticle building units”. This definition points to the need to combine several techniques to distinguish a

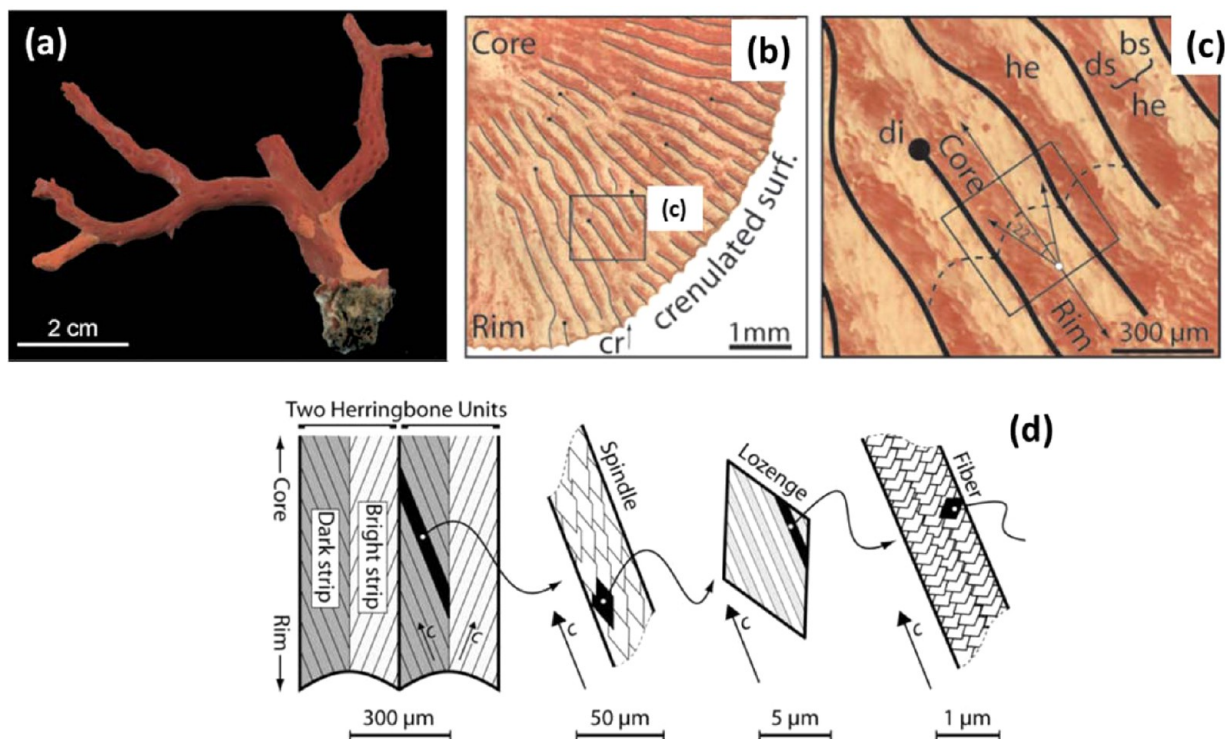


Figure 3. Illustration of six levels of crystallographic hierarchy in the skeleton of the red coral *Corallium rubrum*. (a) Skeleton after partial removal of living tissue. (b) Mosaic structure of a section of the radial arrangement of herringbone units under reflected light microscope (polarized light) with long-range crystallographic order, where (c) shows the enlargement of the rectangular section in (b). Image (c) shows that the herringbone units are made of the association of a dark (ds) and bright (bs) strip (black arrows indicate both the elongation of the spindles and the orientation of the *c*-axes of calcite crystals). Schematic image (d) illustrates the six hierarchy levels. For clarity, some angles and lengths are not to scale. Note that the crystallographic orientation of the *c*-axis is preserved across several hierarchical levels. Image (a) is reproduced from ref 39, and images (b–d) are taken from ref 38, all with permission of the Mineralogical Society of America.

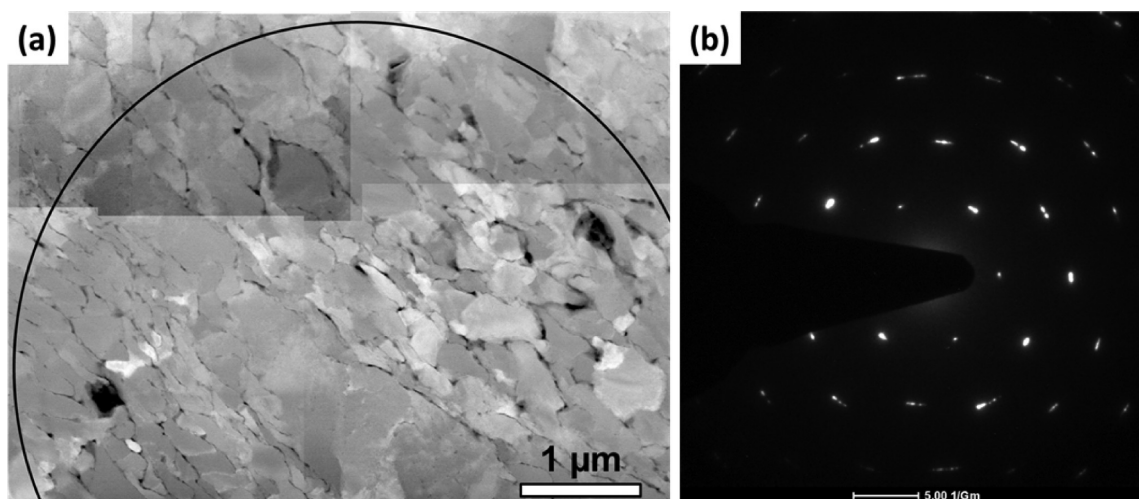


Figure 4. Structural features of red coral. (a) TEM micrograph of submicrometer units in a FIB cut of a red coral sclerite. Gray level variations in the dark field image are due to slight variations in crystallographic orientation. Dark zones between the nanocrystals indicate organic material. (b) Corresponding selected area electron diffraction (SAED) pattern recorded from the marked region in (a). Images are kindly provided by D. Vielzeuf, N. Floquet, and A. Ricolleau (unpublished data).

mesocrystal from other types of crystalline materials, especially single crystals, (e.g., by combining electron microscopy imaging and diffraction techniques) to clearly verify the long-range order at the atomic scale in at least one direction and the existence of nanoparticles in the mesocrystal. Especially the proof of nanoparticles can be problematic.³⁶ Figure 2 schematically illustrates the general concept of mesocrystals

and compares the structural features of different types of crystalline materials.

■ MESOCRYSTALS IN BIOMINERALS AND BIOINSPIRED MATERIALS

Mesocrystals have been found in several biominerals like nacre, sea urchin spines, foraminifera, corals, and egg shells.³⁷ Calcite

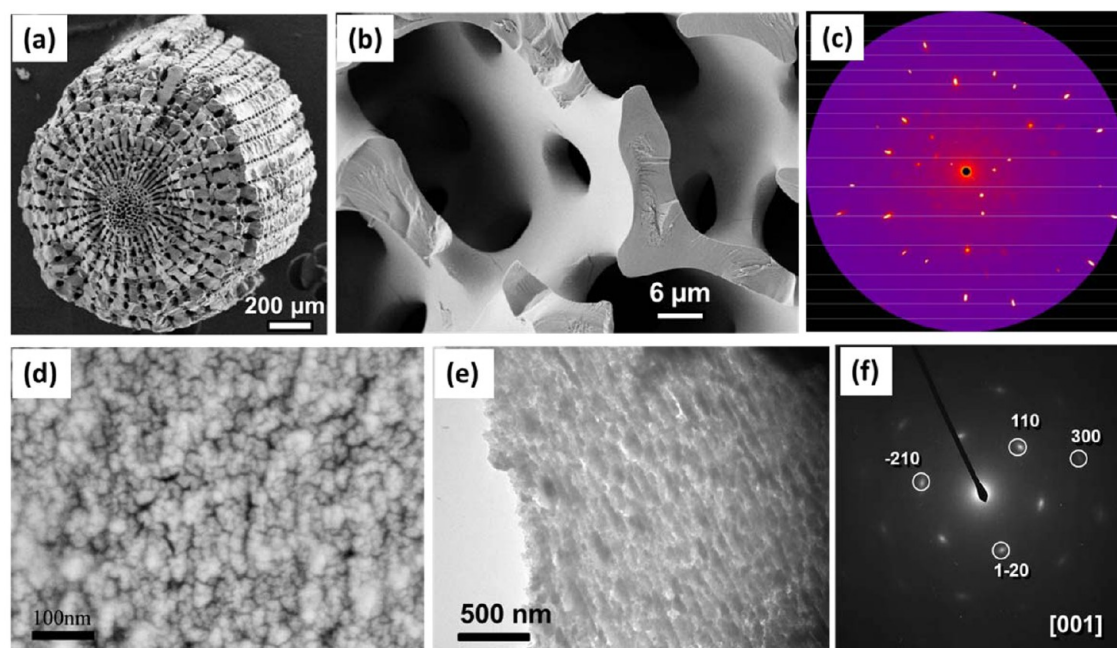


Figure 5. (a, b, d) SEM images illustrating the structural features of a fracture surface of a sea urchin spine shown at different magnifications. (c) X-ray diffraction pattern obtained from the sea urchin spine. (e) TEM image of microtome thin cut showing bright regions in between the calcite nanoparticles stemming from amorphous phase. (f) Electron diffraction pattern recorded from the region shown in (e). Reprinted from Seto et al. (ref 20), National Academy of Sciences USA.

nanocrystals are invariably the building block in these biogenic mesocrystals that often display complex, hierarchical structures with specific functions.

Red Coral *Corallium rubrum*

Red coral is an excellent example of a biomineral that displays a multilevel modular organization.³⁸ Vielzeuf et al. showed by a combination of transmission electron microscopy (TEM) on thin cuts prepared by focused ion beam (FIB) and electron diffraction that red corals contain mesocrystals at the lowest hierarchical level.^{38,39} Figure 3 demonstrates the various hierarchical levels of red coral, including the macroscale herringbone structure down to the spindles and fibers at the nanoscale. The TEM images in Figure 4 show that the mesocrystal consists of submicrometer crystallites that are separated by thin regions with organic material (black lines in Figure 4a). The sharp electron diffraction pattern in Figure 4b shows that the submicrometer calcite crystallites are in crystallographic alignment, which together with the TEM evidence of separate nanocrystals proves that red coral contains mesocrystals. Electron backscatter diffraction (EBSD) also proved that the calcite nanocrystals have a similar orientation over areas larger than one square micrometer.³⁸

Sea Urchin Spine

Sea urchin spine is another remarkable biomineral that in essence is a mesocrystal. Its combination of a spongy structure on the microscale (Figure 5a, b) with a single crystalline behavior (Figure 5c, f) has fascinated and challenged researchers over decades. In fact, it was debated whether sea urchin spine is a single crystal according to X-ray diffraction or polarization microscopy results or polycrystalline due to its conchoidal fracture behavior. This debate could only recently be resolved when it was shown that the sea urchin spine is a mesocrystal.²⁰ Figure 5d–f demonstrates that a sea urchin spine consists of a bricklike structure of polydisperse single crystalline

calcite nanoparticles with a slight crystallographic misorientation (electron diffraction spots with slight arcs) surrounded by a bright region of amorphous phase. The angular spread in Figure 5f is probably increased by the microtome cutting, since noninvasive nano-XRD rastering of a $50 \times 50 \mu\text{m}^2$ area revealed a misorientation of $<1^\circ$, suggesting that the nanoparticle orientation in the mesocrystal is almost perfect.²⁰ The dimensions of the nanoparticles in Figure 5d,e were confirmed by SAXS/USAXS utilizing the amorphous phase/calcite contrast.²⁰

The amorphous phase was quantified by solid state NMR (not shown) to be a ca. 2 nm thick layer in between the polydisperse calcite nanobricks. It can be speculated that this amorphous inorganic layer fulfills a similar function as the organic layers around the calcium carbonate crystals in nacre, which contribute to the very high fracture toughness. Because seashells and sea urchin spines serve to protect the organism, enhanced fracture toughness by a mesocrystalline structure would indeed be evolutionarily beneficial for these organisms.

■ BIOMIMETIC SYSTEMS

To date, many strategies have been developed for the synthesis of biomimetic analogues of several natural biominerals. Most investigators target to produce biomimetic composite materials with the aid of synthetic or natural polymers. The morphological and/or structural relations between the biomimetic and biogenic materials are highlighted with an aim to provide insight into the basic principles of nucleation, self-organization and formation of hierarchical composite materials. In this Account, we highlight some of the structural features of mesocrystals presented in recent studies of such biomimetic systems.

Fluorapatite-Gelatin Mesocrystals

Fluorapatite-gelatin nanocomposites grown by double-diffusion in gelatin gels represent one of the fascinating examples of

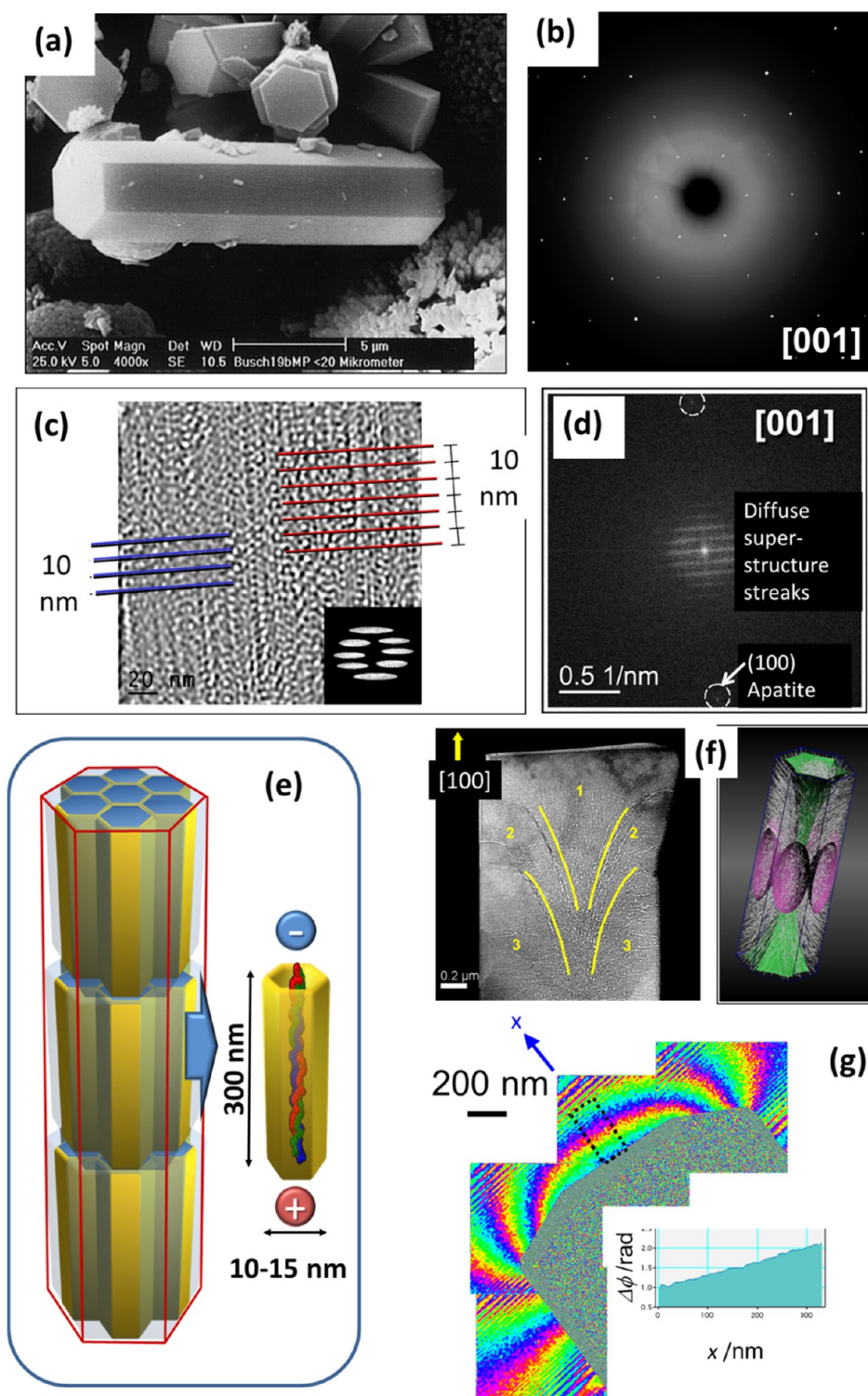


Figure 6. Experimental observations and simulations of a fluorapatite-gelatin nanocomposite. (a) SEM image of hexagonal prismatic crystal-like entities of fluorapatite-gelatin nanocomposite. (b) X-ray diffraction pattern (WAXS) of a specimen with a habit as shown in (a). (c) Filtered HRTEM image (along [001]) of the ordered arrangement of defects (periodicity 10 nm) originating from the incorporation of the gelatin macromolecules. (d) Superstructure in the FFT of the HRTEM image characterized by diffuse streaks near the primary beam (small angle region in diffractogram) with a periodicity of about 10 nm and multiples thereof. (e) Sketch summarizing the experimental observations on the structure built up by parallel rod stacking of elongated nanosubunits (fluorapatite grown on the protein triple helix) with their long axes running along [001] of the hexagonal prismatic mesocrystal. (f) (left) TEM image of the upper part of a FIB thin cut parallel [001] of a hexagonal prismatic specimen showing a complex pattern of incorporated gelatin microfibrils (diameter ~ 10 nm); (right) simulated 3D fibril pattern (white lines) revealing the areas separating fibrils with different orientations. (g) Reconstructed phase images of electron holograms showing the electric potential distribution around the corresponding composite aggregate. (Panels (a), (b), and (g) reproduced from ref 30 with kind permission from Springer Science and Business Media. Panels (c) and (d) reproduced from ref 31 with permission of The Royal Society of Chemistry. Panel (f) reprinted with permission from Knip et al. (ref 33), © (2014) John Wiley & Sons.)

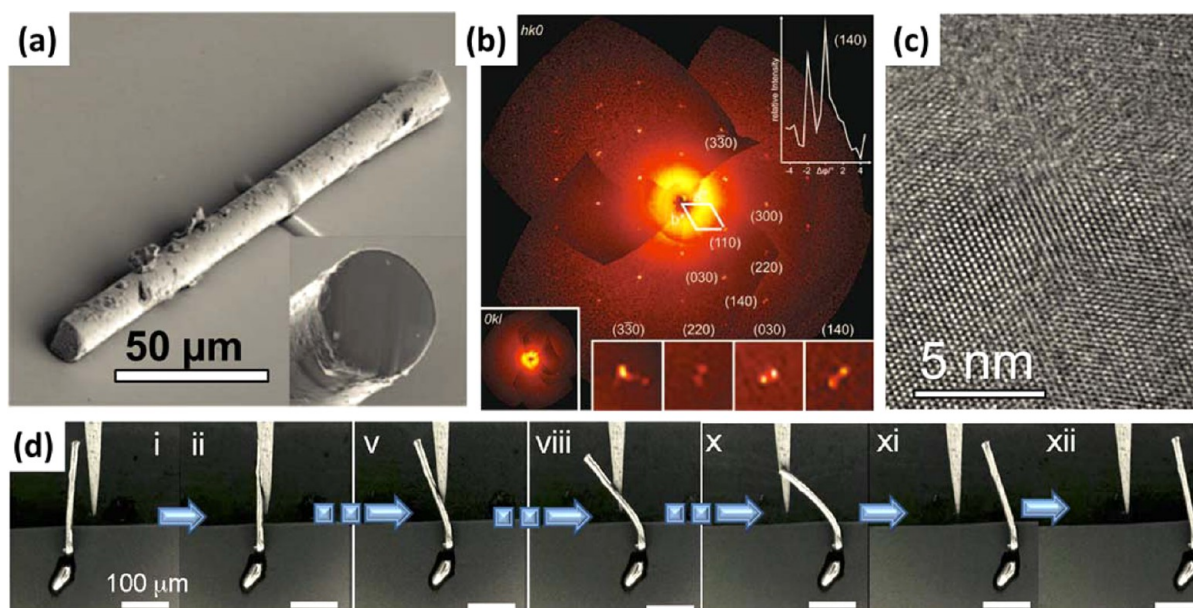


Figure 7. Structural features and mechanical properties of calcite spicules. (a) SEM image of a representative synthetic spicule. (b) X-ray diffraction pattern of the $(hk0)$ -plane of a mature synthetic spicule (aged for 10 months). Zoomed images of some selected reflections (bottom right) illustrate a splitting of the diffraction peaks (due to twinning of calcite crystals). (c) HRTEM image of a cross section of a mature spicule. (d) Time series (i–xii) of SEM images illustrating a bending test with a micromanipulator. The synthetic calcite spicule (7 months aged) does not fracture even under extreme deflection and slowly recovers to its initial shape after the relief of mechanical stress. From Natalio et al. (ref 32). Reprinted with permission from AAAS.

biomimetic synthesis of analogues of apatite-based biomaterials.^{30,33,40,41} Detailed structural characterization of hexagonal prismatic crystal-like entities of fluorapatite-gelatin nanocomposites (containing 2.3(3) wt % gelatin) reveals that the material can be described as a mesocrystal (called mosaic dominated nanocomposite superstructure in the original work) (Figure 6). The wide-angle diffraction pattern (Figure 6b) of the specimen is consistent with a fluorapatite single crystal; however, the small angle region (Figure 6d) of the digital diffractogram (FFT of the HRTEM image along the $[001]$ apatite zone axis) reveals diffuse streaks with a periodicity of about 10 nm (and multiples of this value). By means of high resolution TEM (HRTEM) imaging (Figure 6c), it was shown that this periodicity originates from the organic component (gelatin macromolecules inside the nanoboards) on which the fluorapatite is nucleated.³¹ Therefore, the real inner architecture of the hexagonal-prismatic individuals is consistent with parallel rod-stacking of elongated nanosubunits with their long axes running parallel to $[001]$ as schematically presented in Figure 6e. It has been suggested that the intrinsic electric dipole fields (detected by electron holography (Figure 6g)^{41,42}), generated by the dipolar character of the aligned gelatin triple helix, cause the integration of a meso/macroscale pattern of gelatin microfibrils into the superstructure matrix (Figure 6f)^{43,44} and also control the morphogenesis of fluorapatite-gelatin nanocomposite aggregates. Hence, this example shows that mesocrystals are able to integrate/incorporate foreign components/foreign patterns on a next level of hierarchy without significant distortion of the mesocrystalline structure.

Mesocrystalline Calcite Spicules

Tremel and co-workers recently demonstrated that mesocrystalline calcite spicules can be synthesized using silicatein protein fibers from demineralized glass sponges as a template for very slow calcium carbonate deposition.³² Figure 7a shows that self-

assembled calcite mesocrystals with a high organic content of 10–16 wt % are formed on the protein fiber template. The spicules that are younger than 5 months are amorphous, but they are gradually transformed into a calcite-based composite within several months. Spicules that are older than 6 months display a X-ray diffraction pattern with distinct peaks indicating a crystalline material with a strong preference for $[100]$. Figure 7b shows that the sharp and well-defined X-ray diffraction pattern of a mature spicule (aged for 10 months) corresponds to twinned calcite crystals while the HRTEM images of its cross section in Figure 7c show the presence of small calcite crystals (~ 5 nm) embedded into an amorphous protein matrix, which clearly shows that the synthetic calcite spicules are mesocrystals. Interestingly, Figure 7d shows that the mesocrystalline calcite spicules can sustain a very large deflection without fracture.

This remarkable behavior can be attributed to the mesocrystalline nature of the spicule where each oriented calcite nanocrystalline domain is surrounded by proteins and also a layer of amorphous calcium carbonate, which allow the material to deform without catastrophic cracking or fracture. The structure of the synthetic calcite spicules has much in common with the sea urchin spine structure (Figure 5).

Mesocrystals in Colloidal Arrays

Self-assembly of nanoparticles into ordered structures is a promising strategy for production and design of nanostructured materials with novel properties.^{28,45–47} Indeed, ordered arrays of nanoparticles combine the properties of the nanocrystalline building blocks with the collective properties of the interacting nanoparticles. Nonspherical nanoparticles have attracted increased interest due to the possibility to tune the electronic, optical, and magnetic properties by controlling both the size and shape.^{28,48} Indeed, there is currently a significant activity in this area where recent reports have illustrated how assemblies

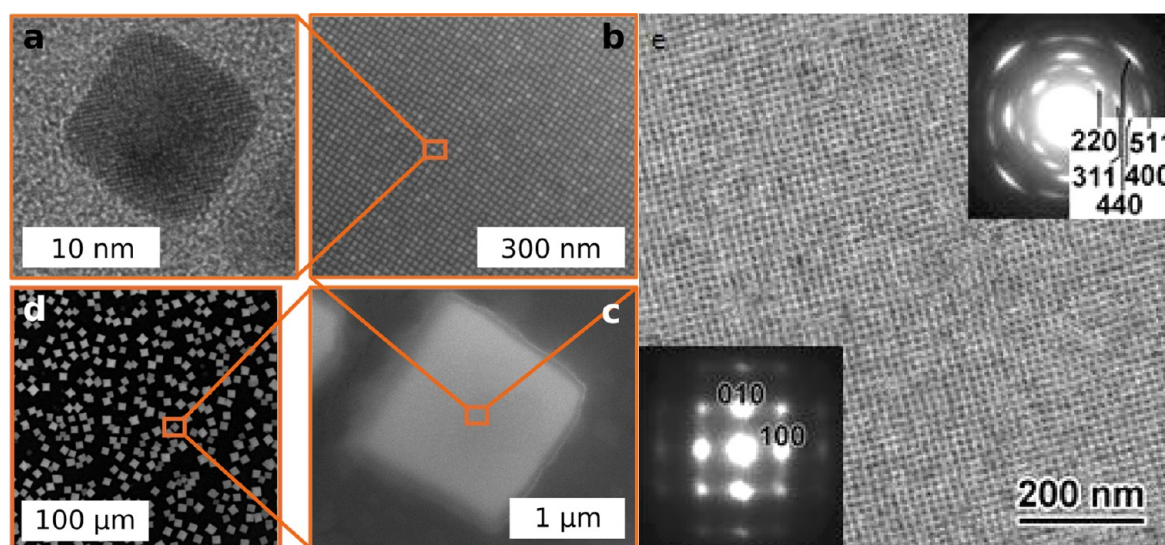


Figure 8. Structural features of self-assembled arrays of iron oxide nanocubes. The image sequence (a)–(d) illustrates the structural features of mesocrystals formed by evaporation-driven self-assembly of iron oxide nanocubes from a toluene-based dispersion with a progressively reduced magnification. (e) TEM image of self-assembled nanocubes with selected area diffraction patterns on atomic (inset, upper right) and mesoscale (inset, lower left). Panels (a)–(d) provided by Michael Agthe. Panel (e) reprinted from Ahniyaz et al. (ref 21), © (2007) National Academy of Sciences USA.

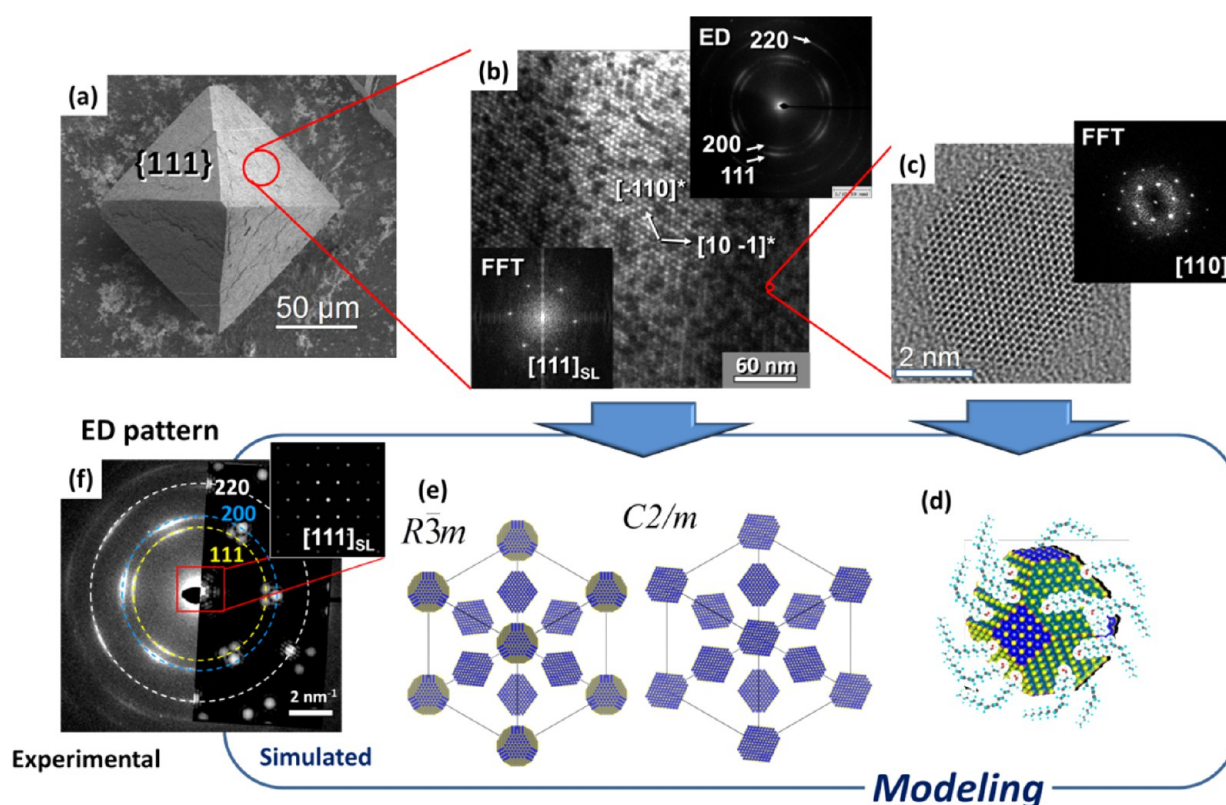


Figure 9. Structural features and simulations on PbS mesocrystals. (a) SEM image of octahedrally shaped PbS mesocrystals. (b) TEM images of FIB-cut viewed along $[111]_{SL}$ with corresponding FFT inset (bottom left) and electron diffraction pattern (top right). (c) HRTEM image of PbS nanocrystal (along $[110]$ zone axis). (d) Corresponding ideal model of truncated octahedrally shaped PbS nanocrystal (as shown in (c)) stabilized by oleic acid molecules. (e) Simulated PbS mesocrystals viewed along $[111]_{SL}$. (f) Comparison of the observed (left) and simulated (right), corresponding to models shown in (e)) ED patterns detected along $[111]_{SL}$ of the PbS mesocrystal, illustrating orientational relationships between the superstructure and the PbS nanocrystal reflections. Figures adapted from ref 22.

with both orientational and positional order, that is, self-assembled mesocrystals, can be produced.^{15,16,18,21,22,47–52}

Iron Oxide Mesocrystals

Iron oxide nanocubes are interesting nanoparticle building blocks that offer the possibility to not only probe the influence

of the nonspherical shape on the resulting structures but also allow the option to induce a directional magnetic dipolar interaction between the self-assembling nanocrystals.^{21,50} Truncated maghemite nanocubes coated with oleic acid have been used to produce mesocrystals with both translational and orientational order by evaporation-induced self-assembly (Figure 8). Depending on the degree of truncation and the conditions during assembly, a rich structural diversity has been observed (Figure 8), including simple cubic,²¹ body centered tetragonal,⁵⁰ and face centered cubic structures.⁵³ All of these structures are characterized by a long-range orientational order, as exemplified by the electron diffraction in Figure 8e, and also a long-range translational order of the assembled nanoparticles. Hence, these mesocrystals exhibit an additional degree of order compared to most of the previously described biomineralized mesocrystals, which relates to the packing of the monodisperse polyhedral nanocrystals.

PbS Quantum Dot Mesocrystals

PbS-based nanoparticle superlattices are interesting due to their size-dependent, tunable optical properties, which make them a prime candidate for applications in the field of infrared optoelectronics and photovoltaic applications.⁵⁴ Recent studies have shown that oleic acid coated PbS nanocrystals form faceted colloidal assemblies that in fact are mesocrystals (Figure 9a).²² Structural characterization of the PbS-mesocrystals on different length scales using X-ray and electron diffraction, scanning electron microscopy, and high-resolution transmission electron microscopy shows a long-range translational order of the nanoparticles (size ~ 5.5 nm) within an fcc superlattice ($a_{\text{SL}} = 15.4$ nm) with a single crystal like diffraction pattern in the small angle region (Figure 9b). This feature is combined with a textured diffraction pattern in the wide-angle region (Figure 9b), which stems from a specific crystallographic orientation of the truncated octahedrally shaped PbS-cores (Figure 9c, d). Based on the experimental data, a series of atomistic models was developed describing the multidomain structure of the mesocrystals (Figure 9d).²² Systematic analyses of the orientational relationships between the truncated octahedrally shaped PbS nanocrystals within the fcc superlattice array indicate that the nanoparticles have a tendency toward face-to-face interactions within each closed-packed layer (resulting in a $[111]_{\text{SL}} \parallel [110]_{\text{PbS}}$ crystallographic orientational relation), while keeping a certain degree of orientational mismatch. Furthermore, it was shown recently that these structural features are already prearranged in the 2D state of nanoparticle self-assemblies.⁵⁵

Platinum Nanocube Mesocrystals

Truncated platinum nanocubes with a narrow size distribution that are coated with octylamine have been assembled into well-ordered mesocrystals with different structures (see Figure 10). Nanocubes with an edge length of $l \approx 5.5$ nm and low degree of truncation⁵⁰ $\tau \approx 0.25$ – 0.3 assembled with a primitive cubic mesostructure with a lattice parameter $a_{\text{MS}} \approx 6.6$ nm. Alternatively, nanocubes with $l \approx 4.7$ nm and $\tau \approx 0.4$ assembled into a pseudo-fcc structure with $a_{\text{MS}} \approx 11$ nm.⁵⁶ The wide-angle diffraction pattern of the cubes in the primitive cubic structure (Figure 10 top, left inset) indicates that the nanocubes possess a long-range order at the atomic level in the three directions with the (100) facets parallel to the substrate. Alternatively, the wide-angle diffraction pattern of the truncated nanocubes (Figure 10 bottom, left inset) suggests the coexistence of truncated nanocubes also aligned in 3D with

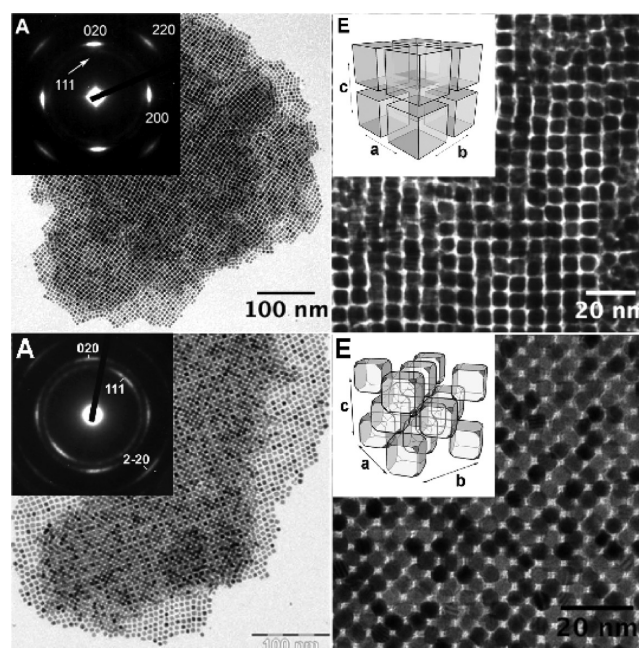


Figure 10. Mesocrystals formed with platinum nanocubes with low (top) and medium (bottom) degrees of truncation shown at low (left) and medium (right) magnifications. The insets show (left) the wide-angle diffraction patterns of the mesocrystals and (right) the proposed packing arrangements. Reprinted with permission from ref 56. Copyright 2008 American Chemical Society.

the $[100]$ direction normal to the substrate together with a fraction of particles with what seems the $[110]$ direction normal to the substrate. It is worth noticing that the interparticle distance in the primitive cubic mesostructure is smaller than the length of an extended octylamine molecule (≈ 1.5 nm), indicating a considerable interdigitation, whereas in the case of the pseudo-fcc mesostructure, the interparticle distance is similar to the length of the alkyl chain. The differences could be related to the both the particle packing and the magnitude and type of the interactions between the cubes: in the primitive structure there, are six nearest neighbors in a face-to-face configuration, whereas in the pseudo-fcc structure there are eight nearest neighbors in what can likely be described as a corner-to-face configuration. Modeling using averaged force fields and atomistic molecular dynamics simulations suggest that the truncated faces possess electric dipoles generated by the charge transfer between the octylamine ligands and the platinum cores. The presence of dipoles on the nanocubes was suggested to result in multipolar Coulombic coupling that favors a centered packing (pseudo-fcc) over the primitive one.⁵⁷

CONCLUSIONS AND OUTLOOK

In this Account, we have given a comprehensive definition of mesocrystals together with a description of the requirements for their characterization. It is important to emphasize that the mesocrystal definition is purely structural and does not imply how the mesocrystals are formed. Mesocrystals can be porous or space filling with amorphous inorganic or organic matter separating the crystallographically oriented nanocrystals.

The structural features of mesocrystals in three different types of inorganic materials, biomineral, biomimetic composites, and colloidal arrays, have been presented. The examples have only been selected from systems within the three types of

materials where the necessary detailed structural characterization has been reported. However, it is clear that mesocrystals exist in many more systems and that the mesocrystal definition also could be useful to describe how crystalline (bio)polymer systems are organized. For example, the structural polysaccharides chitin and cellulose form crystalline nanorods that can organize into superstructures with well-defined order.⁵⁸ Other macromolecules are borderline cases; protein crystals, for example, are not mesocrystals because the protein building unit itself is not a nanocrystal. Deposited laminated thin films generated by chemical vapor deposition or atomic layer deposition, where each crystalline layer with submicrometer thickness is oriented with respect to each other, could also qualify as mesocrystals. But liquid crystals composed of nanocrystals are not mesocrystals since they usually lack the sufficient degree of long-range atomic order, although they can be transformed into mesocrystals.⁵⁹

Mesocrystals are usually but not always a hybrid between an inorganic nanocrystalline phase and an organic or inorganic amorphous material. We have shown that the crystallographic alignment and the composite structure are essential for the impressive combination of stiffness, hardness, high strength, and large flexibility found for many biominerals and biomimetic composites. Controlling the properties and composition of the amorphous layer and the nanocrystal opens up large possibilities to tune the mechanical, electronic, thermal, magnetic, and optical properties of mesocrystalline biomimetic composites and colloidal arrays. Producing mesocrystals by self-assembly of nanocrystals with a well-defined size and nonspherical shape into arrays with a long-range mesoscopic order is of particular interest to explore and tune to utilize the often anisotropic collective properties, for example, magnetic and optical, that extend beyond those of the individual nanoparticles. It is therefore not surprising that mesocrystalline structures are increasingly investigated for materials applications,^{16,18,47} and the great potential of mesocrystals is just beginning to be explored.

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