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Recent Progress in the Replication of Hierarchical Biological Tissues

Oskar Paris, Gerhard Fritz-Popovski, Daniel Van Opdenbosch, and Cordt Zollfrank**

Bioinspired materials research is a continuously growing field in interdisciplinary materials science and engineering with large potential for novel functional materials. One possibility of combining the hierarchical structure of natural materials with the broad range of available constituent materials is biotemplating, i.e., the use of biological materials as scaffolds or casting molds for the synthesis of ceramics, semiconductors, metals, polymers or composites thereof. However, the replication of structural details of complex biological tissues over several levels of hierarchy down to the nanometer level is still a big challenge. The biological templates need to be (made) accessible for the precursor materials down to the nanometer scale, and the desired inorganic replica often require a final thermal treatment with the danger of collapse of the nanostructure. Here, some of the current knowledge about the replication of hierarchical biological materials into ceramics or carbons with special emphasis on wood as a template is reviewed. It is concluded that real hierarchical replication down to the nanometer scale requires a careful preparation of the biological template, followed by elaborate template infiltration via gas or liquid phases and their transformation into a solid, and finally, the gentle removal of the template. Not surprisingly, retaining the replicated material in an amorphous or nanocrystalline state is a key requirement for a successful nanometer-scale replication of biological materials.

1. Introduction

Inspired by nature's main strategy of imparting function to a material, a current trend in materials design and production is to fabricate multi-component materials with hierarchical structure and resulting hybrid functions.[1–6] Many desirable properties including stimulus response, adaptation, or self repair[7] are readily found in biological tissues, which have been optimized by evolution. In nature, the limited availability of elements is compensated by multiscale hierarchical structuring from the nanometer scale to macroscopic dimensions.[8,9] The properties of the resulting materials can differ considerably from their unstructured equivalents, providing protection,[10,11] actuation,[12,13] materials transport,[14,15] movement,[16–18] and the means for catching prey.[19,20] Current state of the art manufacturing techniques can be based on top-down methods which do, however, not allow the easy and cost efficient fabrication of nanometer-scaled structures. On the other hand, bottom-up self-assembly of atomic or molecular building blocks is typically limited to structural sizes way below the micron length scale. Therefore, the unattainable structures and multifunctional properties of nature's hierarchical materials[9] have outperformed human-made materials for millennia. Nevertheless, these purely organic materials or organic/mineral composites are often of limited use for high-performance engineering applications, for instance, if high temperatures or aggressive chemical environments are envisaged. Hence, the promise of bioinspired materials design is to investigate and to employ biological materials synthesis and structural solutions in order to develop strategies for the creation of advanced functional materials. There are essentially two ways to achieve this goal. The first way is to extract a functional concept or a design strategy from a biological material and to use this information to fabricate a synthetic material or device. This material or device may exhibit similar structural elements, and therefore show functional properties resembling those of the original biological system. Alternatively this approach may—through abstraction—also result in novel compounds and composites incorporating only selected structural elements or engineering solutions of the natural prototype. Often, only the idea is used to create a certain function which might even be different from the original one. Along these lines, nature can be seen as a pool of ideas to inspire alternative materials design and to provide novel routes in materials processing. Prominent examples which are already commercialized are the hook-and-loop fastener, branded Velcro, which is based on burdock (*Arctium*) hooks,[21] self-cleaning materials based on Lotus leaf surfaces,[22,23] or adhesive materials based on the Gecko feet structuring.[18,24,25] More recent examples include tough ceramics using nacre as an inspiration source,[26–28] hydrodynamic surfaces inspired by shark skin,[29,30] concepts to create motion by mimicking plant actuation,[13,31] or even combined features.[32]

Prof. O. Paris, Dr. G. Fritz-Popovski
Institute of Physics
Montanuniversitaet Leoben
Franz-Josef-Str. 18, 8700 Leoben, Austria
E-mail: oskar.paris@unileoben.ac.at
D. Van Opdenbosch, Prof. C. Zollfrank
Fachgebiet Biogene Polymere
Technische Universität München
Schulgasse 16, D-94315 Straubing, Germany
E-mail: cordt.zollfrank@tum.de

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Such approaches have been termed bioinspired materials research,[33] biomimetic materials research,[34] or bionics.[35,36]

The second route, on which this Feature Article is focused, is based on a radically different approach, namely the direct use of a biological material as a scaffold or as a casting mold for the synthesis of inorganic materials. Here, the biological material is used as a template for liquid or gas infiltration of a precursor, combined with further chemical or thermal treatments. As outlined in the following chapters, there are several motivations and methods to utilize natural templates. These methods are collectively referred to as biotemplating[37] although other terms such as biomorphous materials[38,39] or biomorphic mineralization[1] have been used.

2. Definition and Strategies

A widely employed synthesis method for advanced functional materials is the formation of inorganic ceramic or hybrid ceramic/polymer structures using biological templates. A natural equivalent to this process is the petrification of organic substances under the influence of mineral-forming salts in aqueous solution.[40,41] The resulting structures were observed by Hooke more than 300 years ago.[42] The use of natural templates is a rediscovered,[43,44] commonly applied method in contemporary materials chemistry to synthesize novel structures from the macroscopic down to the nanometer length scale.[45,46] First approaches to replicate the structure of wood for instance[47,48] showed interesting mechanical properties of the resulting inorganic materials, soon leading to an increasing interest in this field of research. Since then, a large variety of inorganic structures that are currently unattainable through any other method have been prepared.[1,4,5,49]

Almost any organic material and structure such as low molecular weight polymers, supramolecular assemblies, viruses, cells, cellular- and extracellular tissues, or even microorganisms may act as templates. The natural template imposes structural constraints for the material formation during processing. Biotemplating consequently can be defined as (negative or positive) transcription of the organic precursor structure into an inorganic material. This process involves three principal steps: i) template preparation, ii) inorganic material deposition into or onto the template and iii) removal of the template (**Figure 1**).

The template preparation can include removing constituents of the natural structure,[50–54] substitution of surface moieties,[55–58] or deposition of coupling agents.[59–65] Material is deposited by liquid or vapor phase infiltration of the templates[66–68] with reactive or non-reactive melts,[66,69–71] solutions,[54,72,73] colloids,[74–76] or suspensions. Applying vacuum during the infiltration can be beneficial for the removal of air and improves the subsequent filling of pores with the precursor. The template can be removed thermally,[54,77] biologically,[78,79] or chemically.[43,44] The intermediates of these three steps are the pre-treated functionalized templates and organic-inorganic hybrid materials, which may already exhibit interesting potential for applications.[80,81] After the final template removal, an inorganic porous material with a morphology directly related to the organic template is obtained.

Oskar Paris studied Physics at the University of Vienna and received his PhD in Metal Physics from the University of Vienna in 1996. He worked as a postdoctoral research fellow at the ETH Zürich, and as a senior scientist at the Montanuniversität Leoben where he obtained his teaching qualification (habilitation) in Materials Physics in 2003. From 2003–2009 he was a group leader in Professor Peter Fratzl's Department of Biomaterials at the Max-Planck-Institute of Colloids and Interfaces in Potsdam. Since 2009 he is full Professor of Physics and Chair of the Institute of Physics at the Montanuniversität Leoben. His current scientific interests are on the structure and properties of functional nano-composites and nanoporous materials, including biological and biomimetic systems. He is an expert in structure characterization based on scattering methods using synchrotron radiation X-ray and neutron facilities.

Cordt Zollfrank studied Chemistry at the Technische Universität München (TUM), and received his PhD in Forest Science with special emphasis on chemical aspects at TUM in 2000. He worked as a postdoctoral research fellow and later on as a group leader at the University of Erlangen-Nuremberg in the Department of Materials Science and Engineering - Glass and Ceramics. In 2009 he obtained his teaching qualification (habilitation) in Materials Science. In 2011 he accepted the position as a Professor for Biogenic Polymers at the TUM and the Science Center for Renewable Resources in Straubing. His research work is focused on bioinspired synthetic methods for innovative structural and functional materials. A key-area of his work is the formation of biogenic (polymeric) structures and their conversion to composite materials for engineering and biomedical applications. The fundamental chemical and physical transformation processes involved in these conversions are investigated at each level of structural hierarchy.

One of the remaining big challenges in biotemplating of complex hierarchical structures is the structure preservation over several length scales down to the nanometer regime. In the majority of approaches reported in literature, the focus was set pragmatically to a particular length scale. This was typically the micrometer to sub-micrometer (Sections 3.1 and 3.2), or nanometer scale (Section 3.3). The preservation of structural hierarchy down to the nanometer scale by heat treatment of natural materials is reviewed in Sections 4.1 and 4.2. In Section 5, pathways to a true replication of the entire hierarchical structure of natural materials are presented.

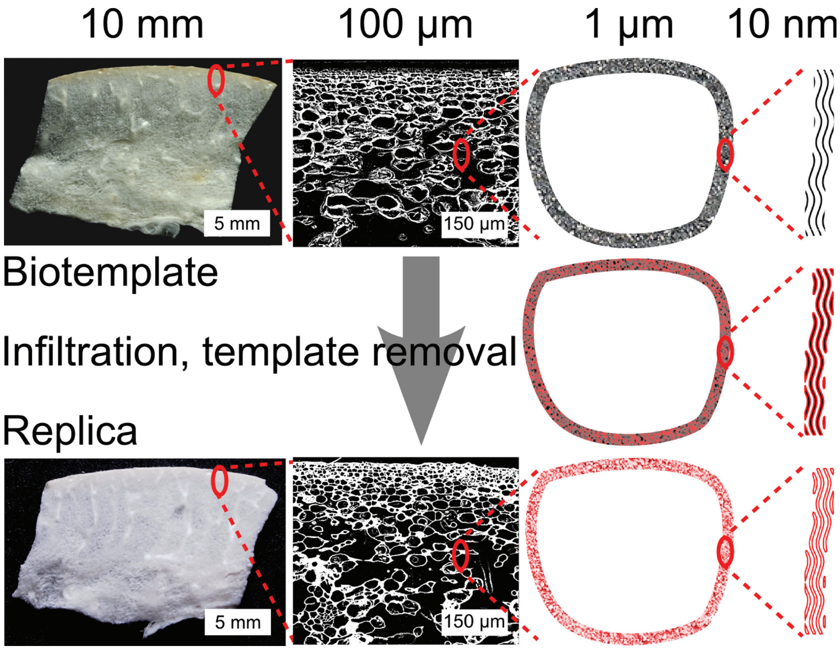

Figure 1. Example of a nanometer-precision biotemplating process. Several hierarchical levels of a biological template material are shown for the example of a pomelo peel[77] (upper row). From left to right. Photograph, SEM micrograph, sketch of a single cell wall in cross section, and sketch of the cellulose fibrils in longitudinal section. After infiltration of a suitable inorganic precursor and selective removal of the template, a replica of the nanostructure with pores replacing the original cellulose fibrils is created. Ideally, the entire hierarchical structure up to macroscopic length scales is preserved by this process (lower row), leading to an intricate complex material not producible by any other means (see Section 5).

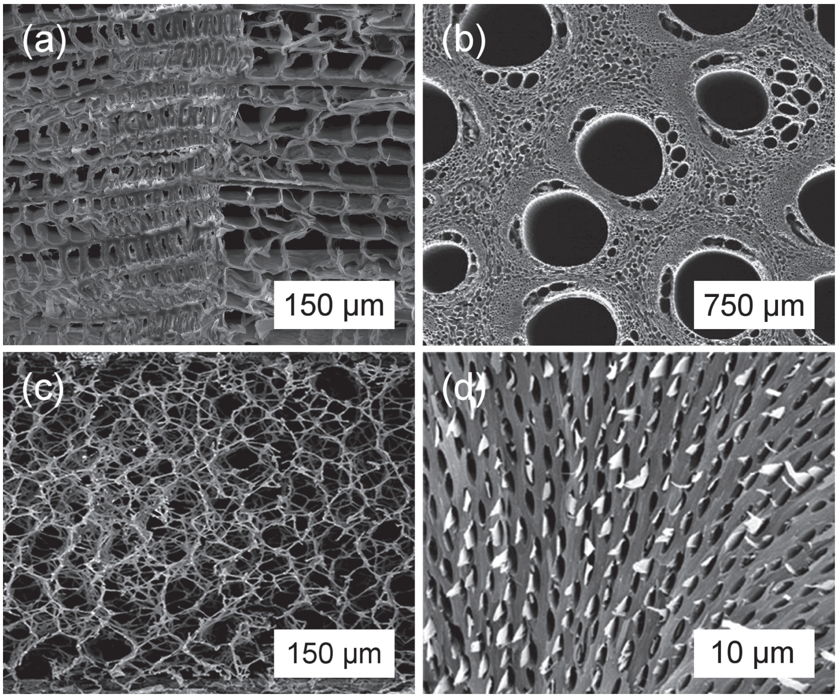

Figure 2. Variety of natural materials with structures observable on the micrometer scale. a) softwood, b) rattan, c) soft rush regular foam, and d) lobster cuticle. d) Adapted with permission.[86] Copyright 2008, Wiley-VCH.

3. Replication of Particular Length Scales

3.1. Biomorphous Materials

The most prominent and extensively investigated level of hierarchy in natural materials is arguably the micrometer scale. It can be observed comparatively easily by light- or scanning electron microscopy and offers a wide range of structural features such as directional porous cells of varying size and shape,[82–84] gradient foams,[85] or plywood-like arrangements,[86] **Figure 2**. Accordingly, many plants such as wood, rattan,[87,88] soft rush[89] or leafs,[90] as well marine animals such as sea-urchin exoskeletons,[91] and single cellular organisms such as diatoms[92] have been used as biotemplates to replicate their micrometer and sub-micrometer structures.

The most extensively used template for micrometer scale replication is softwood, owing to its quite uniform directional cellular structure (see Section 4.1). The resulting materials were often termed biomorphous ceramics.[38] Biomorphous alumina, titania, and zirconia were suggested as filters, catalyst carriers, and highly porous insulation materials.[93–96] Fluorescent materials with cellular structures such as europium-doped barium fluorobromide, strontium aluminate or yttria have also been prepared by wood-templating, and showed improved imaging properties compared to dense imaging plate materials.[72,73,97] The cellular structure of wood has been found to improve the mechanical properties of silicon carbide,[48,98,99] or titanium carbide[100] based ceramics, leading to anisotropic mechanical properties, and remarkably, to a reduction of the probability for catastrophic failure. Wood-based cellular silicon carbide was also assessed as a bone implant material.[101] Besides native wood, some authors also used structured materials derived from natural lignocellulosic materials such as fiberboards.[102,103] Along similar lines, pre-ceramic papers were fabricated from pulp fibers loaded with oxide or carbide particles.[104] High temperature treatment of oxide-loaded paper in air resulted in highly porous products biotemplated by the pulp fibers, whereas carbide-loaded papers yielded dense composite materials after reactive infiltration processing. The anisotropic characteristics of machine-fabricated pre-ceramic paper could be transferred into resulting ceramic composites exhibiting the same anisotropic mechanical features.

Diatoms comprise another class of interesting natural templates that were extensively studied and transformed into a variety of different ceramics, semiconductors, and metals, for potential applications as diverse as sensors, electronics, optics and biomedicine.[105–109] Diatoms are unicellular algae of typically some 10 µm in size. Their cell walls, called frustules, are hard biological templates consisting almost exclusively of silica. Transformation of the frustules into other materials typically requires a high temperature reaction with a gaseous or liquid precursor material. Sandhage et al. have shown that gas/silica reactions allow to obtain MgO[105] and TiO_2[107] with the detailed structure of the diatom frustules being preserved well below 1 µm. Other authors used the TiO_2 replicas of diatom frustules in a further reaction with liquid precursor phases to transform them into perovskites.[110] The reaction $2Mg(g) + SiO_2(s) \rightarrow 2MgO(s) + Si(s)$ at temperatures above 650 °C was shown to produce nanocrystalline mixtures of MgO and Si. After selective removal of the MgO phase, an interconnected network of silicon nanocrystals fully retaining the 3D diatom morphology was obtained.[92] Further processing of this pure silicon material using an electroless deposition approach allowed to obtain noble metal replicas of the diatom frustules.[108] Also direct (one-step) wet-chemical deposition processes leading to self-supporting pure gold replicas of diatoms have been reported,[109,111] the key here being the proper modification of the rather inert and non-conductive silica surface. **Figure 3** summarizes schematically in a flow diagram of how the siliceous cell wall of diatoms can be transformed into a wide range of functional materials.

Such direct conversion approaches are of course not applicable to soft biological templates. If only structuring on the micrometer to sub-micrometer level is desired in the final material, a common processing approach of soft biological tissues involves the carbonization of the natural template structure to provide a hard, pure carbon template for further processing.[47,112] This typically destroys all nanometer structuring (see Section 4.1), but reduces shrinkage and undesired porosities by evaporation of condensates during further processing. Similar diagrams as in Figure 3 with solid carbon as a starting template may then also be drawn for many soft biological templates, such as for instance for the wood replicas discussed above.

3.2. Replication of Photonic Crystals

Sub-micrometer structuring is an essential feature of photonic crystals for the optical regime. Photonic crystals can be designed and tailored to a variety of applications including antireflective[113,114] and highly reflective coatings,[115] waveguides,[116–118] surface-enhanced Raman scattering,[119] as well as gas, temperature, and pH sensors.[120,121] Fabricating photonic materials requires a complex and very precise structuring on the length scale of 100 nm.[122–126] Their manufacture poses therefore a challenge that has led to the use of techniques ranging from lithographic patterning to sol-gel templating.[127–133] Even though materials with omnidirectional photonic band gaps have been realized technically,[134] the fabrication of true three-dimensional crystalline structures with complete band gaps in the visible regime still remains to be demonstrated.[135,136] However, there are many examples of natural tissues featuring photonic crystal structures since the optical signal transfer plays a dominant role in nature.[137–141] Special photonic structures found in nature include the diamond-lattice and gyroid minimal (D- and G-) Schwartz surfaces.[142–144] Such natural photonic structures can be directly used in sensing applications.[145–148] To enhance their resistance to decay at elevated temperatures or in aggressive chemical environments, inorganic replica were produced using biotemplating strategies.[71,96,149–156] Templating routes using a two-step double inverse replication yielded materials with high dielectric contrasts such as alumina or titania.[96,149,154] Usually, in the first step the structure is negatively replicated with silica deposited by a sol-gel route followed by organics removal via thermal oxidation. The resulting inverse structure is in turn replicated by filling the newly created voids via sol-gel deposition of the final material and the silica template removal with hydrofluoric acid (**Figure 4**).

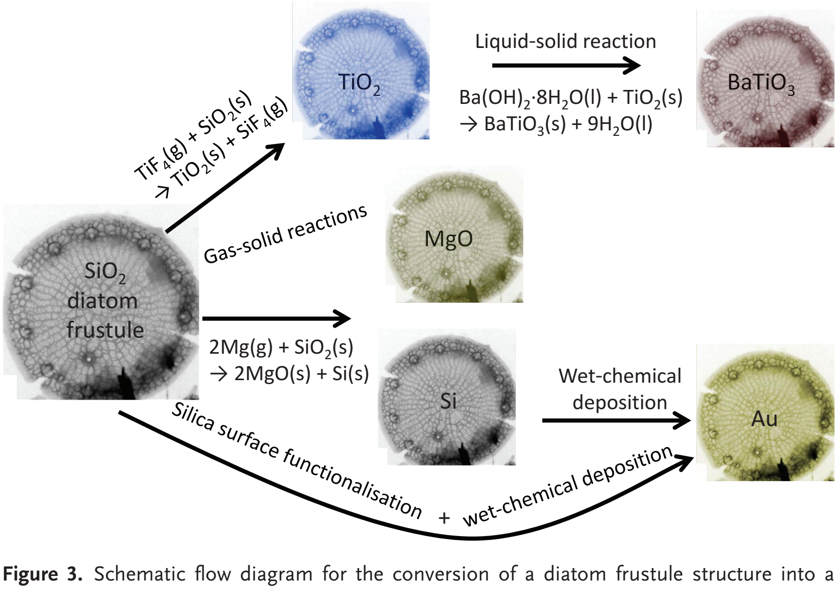

Figure 3. Schematic flow diagram for the conversion of a diatom frustule structure into a variety of different materials while preserving the structural integrity of the system.

One-step replication processes are only practical if the inverse structure offers a useful band gap or is congruent to the original. This is the case for the minimal D-surface in the scales of the jewel beetle *Entimus imperialis*.[157,158] A one-step replication process using siloxane melt infiltration and thermal template removal consequently resulted in D-surface silica replicas.[71] Advantages of this approach are shrinkage- and filling factor control and smooth surfaces of the products, which closely replicate the original structure.[71] Such materials combine stability and durability with the

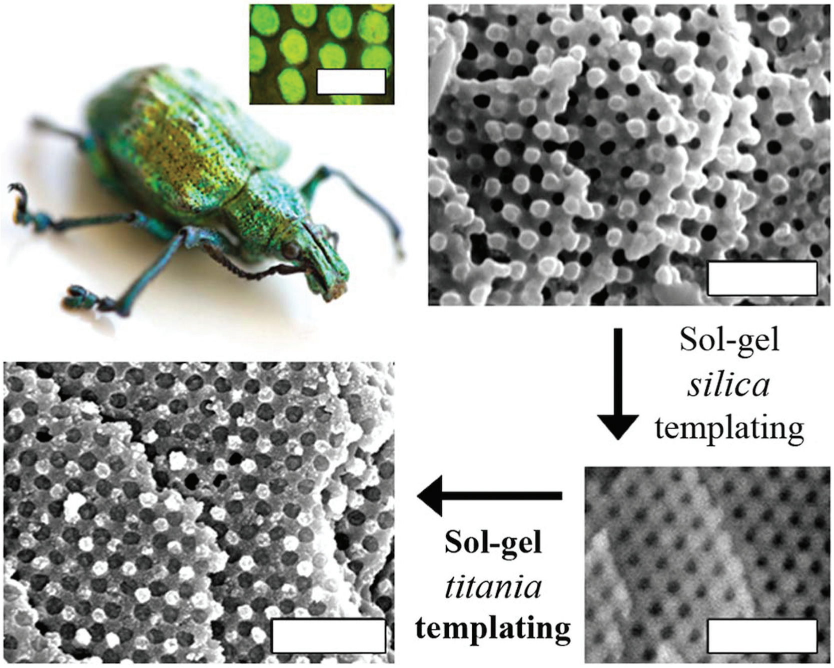

Figure 4. Realization of a two-step double inverse replication of a natural photonic crystal from the elytron of the beetle *Lamprocyphus augustus*. Scale bars are 200 µm for the light microscopy image in the left upper part and 1 µm for the SEM images. Reproduced with permission.[154] Copyright 2010, Wiley-VCH.

fine and intricate structuring that is currently only offered by natural materials. They are therefore promising for the use in sensing or signaling applications under adverse conditions since even small changes in gas- or vapor composition, sample orientation (**Figure 5**), or temperature shift the reflected wavelengths of white-light illuminated photonic crystals.[96,145,146,148]

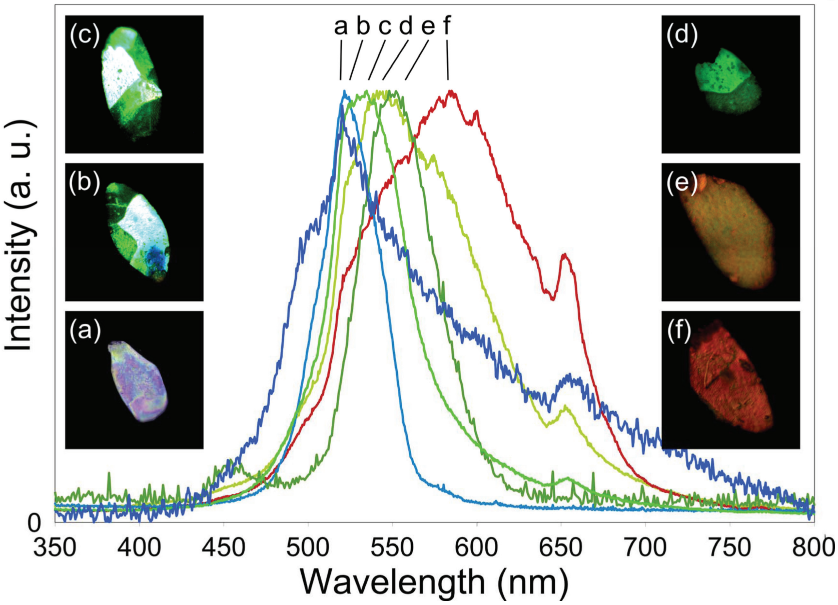

Figure 5. Reflection spectra from a) *Entimus imperialis* beetle scale and b–f) its silica replica in different crystallographic directions. The replica was created in a one-step inverse replication process.[71] The side length of the insets is 150 µm.

3.3. Nanoparticle and Nanofiber Replication

Biological macromolecules such as proteins and DNA, and supramolecular aggregates thereof show detailed and complex structuring on the nanometer scale and have consequently been used extensively as templates for a wide range of nanostructured materials with tailored properties,[1,2,159–161] **Figure 6**. Microtubules or similar cellular protein structures were used to structure metallic nanotubes or nanowires.[162–164] Strands of DNA have been utilized to create conductive nanowires,[165–168] nanoparticle assemblies[169] or two-dimensional nanoparticle arrays.[170] On a larger scale, viruses were used for the guided deposition of nanoparticles,[171,172] formation of cobalt- or iron-platinum nanowires[173,174] or gold-cobalt oxide wires for lithium ion battery electrodes.[175] Viruses were also genetically modified to alter the structures of the biotemplated materials, providing a novel approach to materials structuring.[176] The largest templates showing nanometer structuring are bacteria. These were either directly used, or their exopolysaccharides employed as templates for materials such as magnetic ferrite membranes,[177] zinc oxide photocatalysts,[178] or conducting gold nanoparticle networks.[179] For biotemplating of bacteria, a sonochemical approach can serve both, as synthesis aid and as means of template removal.[180]

Structures based on polysaccharides with hierarchical multiscale ordering and self-assembly properties are promising templates for the formation of patterned inorganic functional and structural materials.[5] Regenerated cellulose nanocrystals have been used as templates for silica nanotubes[181] which exhibited interesting defect-induced luminescence.[182] Similarly, cellulose nanocrystals have been used as templates for the fabrication of gold-coated silica nanotubes which showed a considerable enhancement of Raman signals from deposited materials.[183,184] By a similar route, magnetic nanoparticles[185] and nanotubular aerogels[186] have been prepared. These materials all lack a hierarchical superstructure on the micrometer and meter scale, allowing only for applications in liquid or thin film form.

4. Structure Preservation During Thermal Treatment

The simplest approach to transform a hierarchical biological material into an inorganic replica is by means of thermal treatment of the material at temperatures of at least

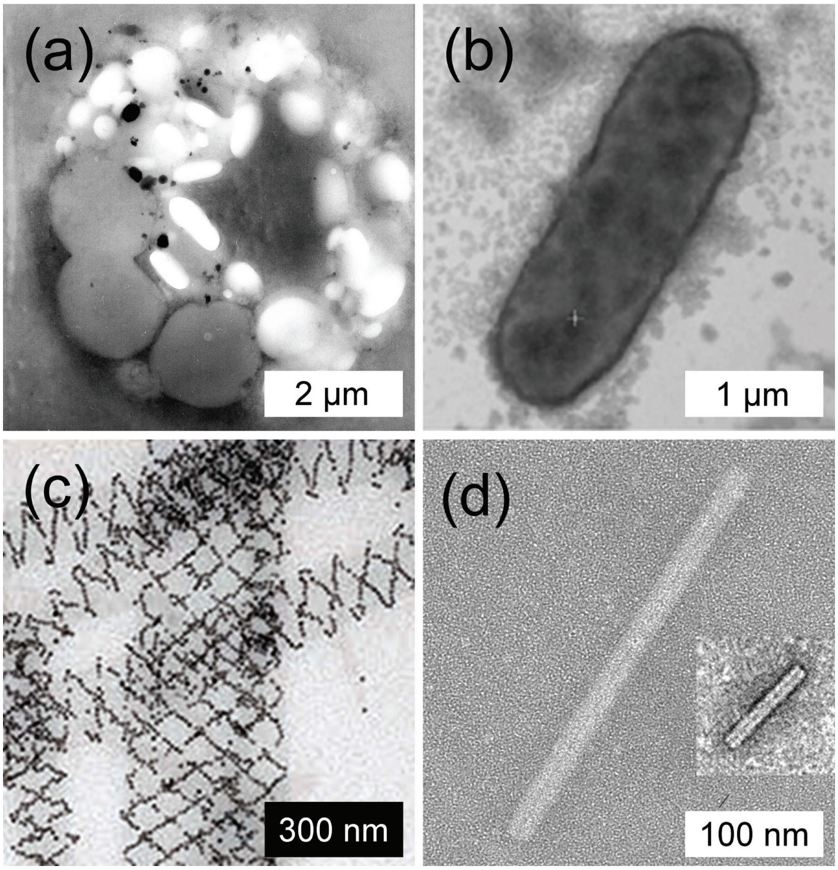

Figure 6. Transmission electron micrographs showing the variety of natural nanoparticles and nanofibers used for biotemplating. a) Alga *Porphyridium purpureum*, b) bacterium *Escherichia coli*, c) synthetic double-crossover DNA,[274,275] and d) tobacco mosaic virus (TMV) with inset: TMV-like particle synthesized from silica-bond RNA strands, width of inset is 150 nm.[276] c) Reproduced with permission.[275] Copyright 2009, American Association for the Advancement of Science. Panel (d) was kindly provided by Prof. C. Wege, University of Stuttgart.

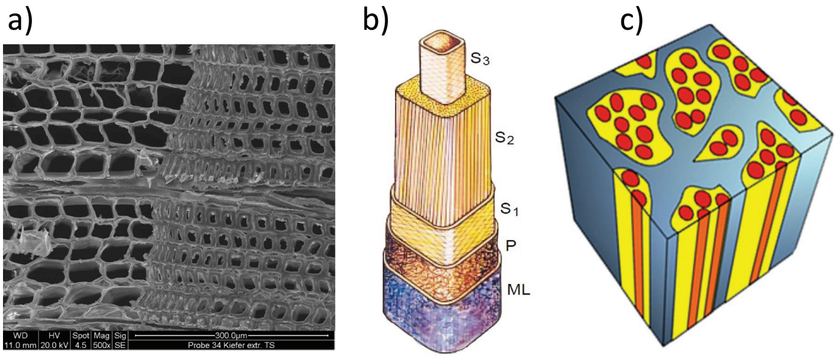

Figure 7. Hierarchical structure of softwood. a) SEM micrograph of the tubular cell structure at the micrometer level. Visible features are the early-/latewood regions with different cell wall thicknesses. b) Sketch of cell wall layers: middle lamella (ML) connecting adjacent cells, primary cell wall, (P) and secondary wall layers (S1-S3; please note that softwoods have only S1 and S2). c) Simplified sketch of the S2 layer nanocomposite structure with crystalline cellulose elementary fibrils (red) embedded in a water-swellable matrix of hemicelluloses (yellow), forming the cellulose fibrils. These are embedded in a lignin matrix (blue). b) Courtesy of Laszlo Jozsa. c) Adapted with permission.[250] Copyright 2012, Wiley-VCH.

400–500 °C. In case of a purely organic structure, heat treatment under the exclusion of oxygen (pyrolysis) transforms the organic material into carbon, which might—at least to certain extend—preserve the structural hierarchy of the template (Section 4.1). If the biological template is mineralized, both pyrolysis (leading to a carbon/mineral composite) or calcination, i.e., thermal treatment in an oxygen rich atmosphere, leading to porous ceramics, are possible (Section 4.2).

4.1. Wood Pyrolysis

Wood is a multifunctional material that is structured on several levels of hierarchy, **Figure 7**. It provides optimized anisotropic mechanical support[187,188] as well as water and nutrient transport.[82] By contrast to hardwoods, the cells in softwoods, which are called tracheids, are only differentiated into early- and latewood, Figure 7a.[82] Softwoods therefore provide a rather uniform template at the micrometer scale and are therefore preferred model biotemplates. On the micrometer scale they show elongated hollow cylindrical tubes of 20 to 40 μm in diameter that are oriented predominantly in the direction of the wood trunk axis.[82,83] Their cell walls are composed of the middle lamella, a primary, and several secondary cell wall layers.[189,190] The secondary cell wall of softwood tracheids is composed of the distinctive S1 and S2 layers, of which the S2 is by far the thickest one, Figure 7b. Several models have been proposed for the spatial arrangement of the dominant wood biopolymers—cellulose, hemicelluloses and lignin—within the cell wall layers. In the S2 cell wall layer, parallel fibrils are arranged helically around the lumen of the tracheid.[191–193] These fibrils have diameters of approximately 10–20 nm,[194] and the angle between the fibril direction and the direction of the tracheid, the microfibril angle, is 3°–5° for normal wood, but can be as high as 50° for compression wood.[195–198] The fibrils themselves consist of elementary cellulose fibrils with diameters of 2–4 nm and hemicelluloses, specifically glucomannan, between the elementary fibrils and xylan at the surface linking the fibrils to the surrounding lignin,[199–202] Figure 7c. These fulfill different mechanical functions as part of the hierarchical nanocomposite wood.[196,203–206]

Charcoal, produced by heating wood to high temperatures under the exclusion of oxygen, has been employed for thousands of years as a fuel.[207] Carbonaceous materials from wood and other lignocellulosic materials have also been used for decades to produce nanoporous activated carbons with extremely high surface areas,[112,208] and bear large promise as inexpensive and renewable resource for functional applications in fuel cells[209] or supercapacitors.[210,211] Pyrolyzed wood has also become of particular interest as a cellular template with micrometer-sized pores to fabricate hierarchically structured ceramic structures with anisotropic properties,[38,48,212] as discussed in Section 2.2. Pyrolysis of wood yields an anisotropic carbon material where the native structure of the wood tissue at the micrometer scale is retained. The anatomical features of the respective wood tissue such as tracheids, medullary rays, bordering pits or traecheas are replicated in the resulting carbon structure in great detail.[197,213] The original cell walls of the tissue are converted into carbon struts. The obtained carbon replica therefore represents an open cellular structure with unidirectional pores corresponding to a positive replica of the former wood cells. Since any plant material can be converted into carbon, the number of accessible structures is only limited by the variety of structures found in nature. The complex internal structure of the composite cell wall is, however, usually not preserved after charring. It is replaced by a homogeneous and structureless carbon phase at pyrolysis temperatures above 300 °C;[197,214] see **Figure 8**. However, the molecular structuring, and orientation as well as the chemical composition of the organic precursor directly affect the degree of alignment and growth of polyaromatic stacks during carbonization.[215] A correlation between oriented, highly crystalline cellulose in Viscose Rayon,[216,217] Lyocell,[218] Ramie[219] and a resulting preferred orientation of the carbon layers with respect to the original cellulose molecular axis was found. Evidence from X-ray diffraction[214,219,220] and Raman microscopy[221] suggest that also in pyrolyzed wood the carbon layers are at least to a small amount oriented with respect to the cell axis. However, the molecular mechanisms transforming the oriented cellulose polymer chains into oriented aromatic carbon rings are still not understood in detail. A "microfibril dominance" model was first introduced by Tang and Bacon[216] and also discussed for pyrolyzed wood.[47,212] Generally, the structural development of the carbonaceous material during pyrolysis has been the subject of a continued scientific discussion in recent years, owing to its importance for potential engineering applications.[47,197,214,219,221–226] Several important stages of structural development during wood pyrolysis can be clearly identified. Up to a temperature of 200 °C, only water evaporation without further chemical or structural changes takes places. At temperatures from 200 to 350 °C, chemical modification—known as torrefaction—of the wood biopolymers occurs, imparting different properties.[227–229] Torrefied wood can be considered an intermediate between the original wood and charcoal.[230] Surprisingly, wood that had been treated at temperatures between 300 and 400 °C, appeared to be completely structureless at the molecular scale, both under the transmission electron microscope[197] and in small-angle as well as wide-angle X-ray scattering patterns,[214,231] Figure 8. This indicates an atomically amorphous solid with no nanometer inhomogeneities up to a scale of several 100 nm. Above 800 °C, disordered carbon with a slightly anisotropic, statistical short-range order

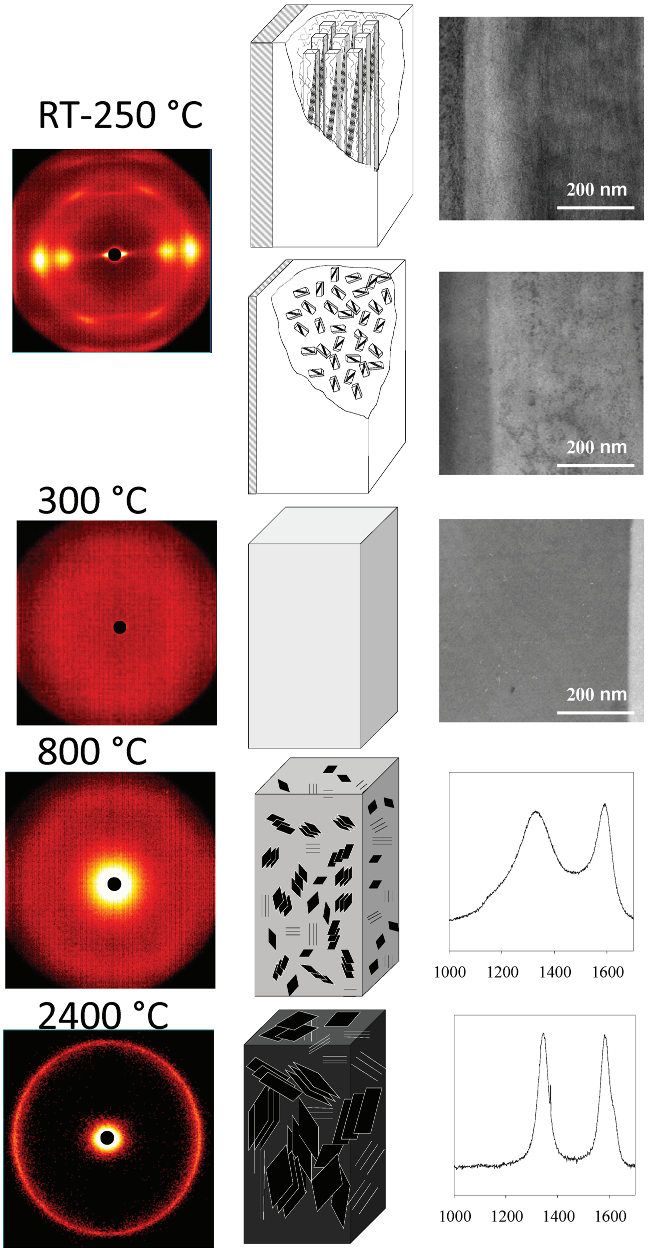

Figure 8. Structure evolution during pyrolysis of wood. Left column: X-ray scattering patterns showing in succession the scattering from crystalline cellulose fibrils in wood, and from amorphous structureless carbon, turbostratic carbon, and highly crystalline graphite, respectively, obtained from the pyrolysis of wood. The scattering angle range is from 0.2°–27° at a wavelength $\lambda = 0.154$ nm, covering the small-angle (SAXS) and part of the wide-angle (WAXS) region.[214] Right column: Transmission electron micrographs (upper three images) and Raman spectra (lower two graphs, x-axis is the Raman shift in cm^{-1}), demonstrating the transformation of a fibrillar structure into a homogeneous, amorphous material during pyrolysis and the growing carbon crystallites at high temperatures. Middle column: Sketch of the proposed nanostructure (size of the box is about 20 nm) illustrating the loss of fibrillar structure, the formation of turbostratic graphite platelets and their crystal growth. Adapted from[214] with permission from Elsevier, and from.[277]

develops. Further ordering towards anisotropic carbon occurs at temperatures higher than 1000 °C;[214,232,233] see Figure 8. The structure becomes highly ordered with a distinct graphitic character when the temperature exceeds 2000 °C. A preferred orientation of the graphite crystallites with respect to the original cellulose fibril orientations could be clearly demonstrated.[214] This is surprising given the fully amorphous and structureless intermediate. Up to now, there is no satisfactory explanation to this "memory" effect during the transformation of crystalline cellulose fibrils into oriented carbon.

4.2. Thermal Treatment of Biomineralized Tissue

The previous section demonstrated that thermal transformation of biopolymers into carbon typically destroys the structuring at the nanometer scale. Continuously biomineralized tissues, on the other hand, can retain an inorganic skeleton during temperature treatment, which may potentially be used as an inorganic scaffold for further biotemplating by infiltration and processing. Plant tissues are typically not mineralized, but there are exceptions. Among the higher plants, members of the genus *Equisetum*, **Figure 9**, are the strongest known accumulators of silica with contents up to 25% of the total plant dry weight.[234–236] A gentle, long-term chemical treatment of the plant stalk with hydrogen peroxide leads to a perfect silica replica of the outer contour of the plant stalk, indicating that the silica forms a continuous (protective[237]) layer at the outer epidermis, Figure 9b. A calcination treatment of *Equisetum hyemale*, optionally after a specific chemical treatment with hydrochloric acid, has a similar effect, Figures 9.[238] Interestingly, a nanoporous silica structure with slit-like pores of 6–7 nm thickness and a BET surface area larger than 400 m^2/g was obtained, suggesting that the combined chemical and thermal organics removal preserves the hierarchical architecture of the original composite structure of the epidermis down to the nanometer scale. The best structure preservation and highest surface area was achieved by calcination at 500 °C. In agreement with findings from silica biotemplating of wood, as discussed in chapter 5, the surface area decreased successively at higher calcination temperatures and the nanoporous structure was fully destroyed at 750 °C when the biogenic silica transformed into crystalline cristobalite.[238]

Similar findings were reported from biomineralized arthropod cuticle. Crustacean cuticle is a complex hierarchical material composed of a chitin-protein nanocomposite reinforced with calcium-based minerals. These are present as calcite in the outermost thin layer of the exocuticle, but mostly as amorphous calcium carbonate and amorphous calcium phosphate.[86,239] Calcination of the cuticle of the American lobster *Homarus americanus* below 400 °C produces a nanoporous amorphous mineral phase with a surface area larger than 100 m^2/g, while retaining the original macroscopic shape and integrity of the sample. Small-angle X-ray scattering revealed that the nanoporous material showed a similar fibrillar nanostructure as the original composite, suggesting that the amorphous mineral phase forms the continuous phase of the fibrous nanocomposite in crustacean cuticle.[239] Consequently, the original hierarchical nanocomposite was transformed by calcination into a porous negative replica, which is open to biotemplating processes by infiltration of the nanometer voids with liquid or gaseous precursors. It is important to note that calcination above 400 °C led to the transformation of the amorphous phase into calcite, with the consequence of the full destruction of the fibrillar nanostructure. Similar observations have also been reported for bone.[240] Calcination of bone at 600 °C resulted in a porous, nanocrystalline carbonated hydroxyapatite. Similar to the processes occurring in lobster cuticle, the degree of crystallinity and the crystallite sizes progressively increased with temperature, while the porosity strongly decreased.

These examples demonstrate that naturally mineralized hierarchical tissues can retain their nanoscale structuring even after the removal of the organic component by thermal oxidation. These findings can be translated to artificially mineralized tissue, as discussed in the next chapter. However, these examples also indicate that high-temperature treatments are generally detrimental in retaining the hierarchical nanostructure

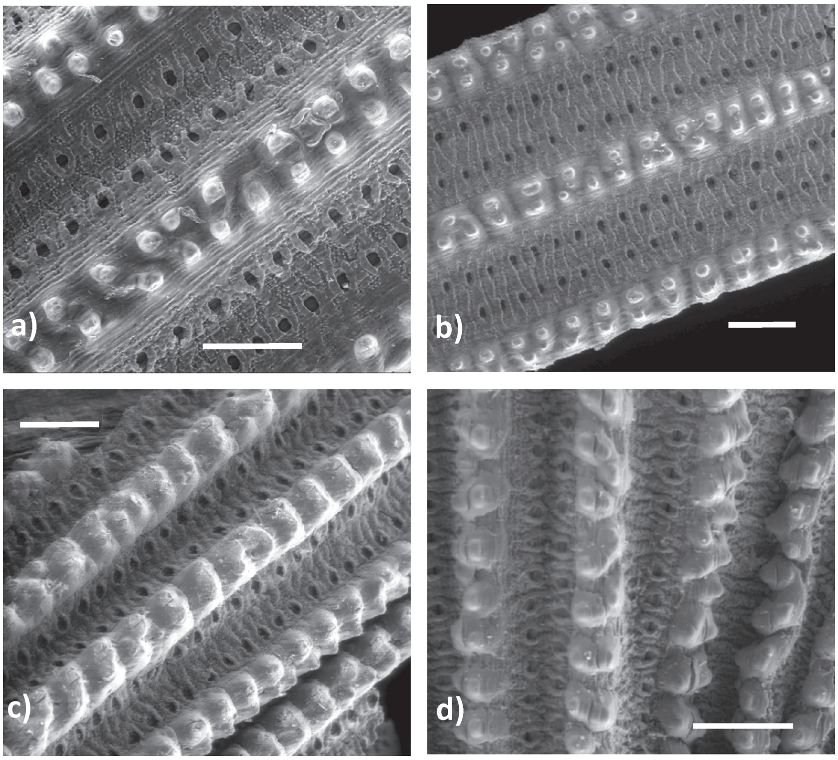

Figure 9. Scanning electron micrographs from *Equisetum hyemale* internodes. a) Native plant, b) sample treated with hydrogen peroxide for 18 months, c) native sample calcined at 400 °C; d) hydrochloric-acid treated sample calcined at 400 °C. The bar is 300 µm in all images. Reproduced with permission.[238] Copyright 2008, American Chemical Society.

during biotemplating. Strong volume changes due to crystallization and crystal growth may entirely disintegrate the nanoporous structure, leading to more or less dense mineral phases with the original hierarchical nanostructure of the template being lost.

5. Hierarchical Nanotemplating of Plant Issue

One particular fascinating property of natural materials is their hierarchical structuring over several levels of hierarchy.[8,9,241] As already shown in Section 4.2, mineralized hierarchical natural materials may retain their nanoscale structuring together with their macroscopic shape and integrity after thermal treatment. Returning to and adapting the templating scheme presented in Section 2, a general pathway for the replication of the entire hierarchical structure of natural materials as sketched in Figure 1 is illustrated in the next section in detail for the hierarchical replication of wood.

5.1. General Templating Strategy for Lignocellulosic Materials

The major processing steps include the proper template preparation, the infiltration of the liquid precursor and its transformation into a solid, and finally the removal of the original template. The choice of the ceramic precursor infiltration method and substances is governed by the pore accessibilities and their wettability. For structural analyses of the template, supercritical drying has been employed to prevent the collapse of the intricate nanometer structuring by drying stresses.[54] In case of fragile, low-density structures, a gradual solvent exchange from water to alcohol has to be performed.[77] An important step in the template preparation for a successful nanometer templating of natural tissue is the removal of low-molecular weight constituents, collectively called extractives. Because of their complex chemical nature,[242] these might react with the chemical substances employed during the templating in an unwanted and irreproducible manner.

If the natural structure does not by itself possess an accessible pore structure, this accessibility must be created either thermally (see Section 4.2) or chemically. In the case of wood, this can be achieved by oxidative removal of the lignin matrix, providing access to the hemicelluloses and cellulose fib rils.[54,243,244] Since the middle lamella connecting the cells is lignin-rich,[245] care has to be taken to keep the tissue intact. It has to be noted that this weakening of the structure at the tissue level by the delignification process is transferred to the final materials. This seriously restricts the fabrication of macroscopic lightweight ceramics from wood with improved mechanical properties, a problem which is unsolved up to now.

The substitution of surface functional groups[55–58] or the use of coupling agents[59–65] greatly widens the range and efficiency of usable precursors by allowing the infiltration of hydrophilic precursors into hydrophobic templates and vice versa. In case of wood, the hydroxyl-carrying, hydrophilic surface of the fibrils[246,247] can be enlarged and acidified by swelling and functionalization with maleic acid anhydride in dimethyl acetamide.[57,69,229] It was shown that this specific treatment led to a swelling of delignified wood by 13% and to an improvement of both the material yield and the replication detail of wood-templated silica.[54]

The choice of precursor systems for nanoscale structure replication is limited by its ability to enter into the smallest spaces found within the structure. Condensing alkoxide solutions have been shown to be very effective precursors for the precise deposition of materials in natural structures.[54,80] By contrast to melt infiltrations, which only fill the cell lumina, they can enter into the cell wall internal spaces, particularly if the sample was previously delignified. The most often used alkoxide is tetraethyl orthosilicate (TEOS) which condenses to pure inorganic silica.[1,67,80,248,249] It is completely miscible with ethanol and can therefore be used in any concentration. In literature TEOS has been used in its monomeric[54,59,74,250] or pre-hydrolysed oligomeric state.[75,76,80,251] Alternatively, alkyl-substituted species were used for a range of purposes such as creating hydrophobic wood composites.[75,80,249,252–254] Alcohols are suitable solvents for the infiltration of alkoxides precursors into plant templates. They are sufficiently hydrophilic to wet the cell walls,[255] but do not prematurely hydrolyze the precursor.[248,256] In case of wood and fruit biotemplating, water localized in the cell walls can act as regioselective condensation agent.[54] A coupling reaction of the infiltrated materials with the cell wall moieties for chemical fixation is deemed desirable to reduce subsequent leaching of the materials from the template, particularly in applied composites.[253,257] The bonding of infiltrated precursors to the natural template can, however, be difficult to prove. In the case of wood, the large variety of already existing bond types[258,259] complicates infrared spectroscopy. The potentially low number of bonded precursor molecules in relation to the total number of molecules can also be below the detection limit of solid state nuclear magnetic resonance techniques.[260]

The template removal by thermal oxidation[54,261] compares favorably to other methods: Compared to chemical removal,[43] it is usually faster. In contrast to very slow biological (e.g., enzymes or fungi) removal,[262] which may be further slowed down by chemical modification of the template,[263] calcination is typically performed in a few hours. Calcination may also serve to oxidize the infiltrated material, which proves particularly important in the case of alkoxide precursors. These typically hydrolyze and condense stepwise,[256] and usually form incompletely condensed, hydroxyl-rich networks. However, if the calcination temperature is chosen too high, crystallization and crystal growth can lead to the collapse of the nanostructure.

5.2. Structural Assessment of Wood Replica

Previous wood replication work has either omitted one or several of the essential template pre-treatment steps, or has employed pre-hydrolyzed or crystallizing precursors, leading to an incomplete structural hierarchy in the products. Nonetheless, typically materials with small particle sizes, textural imprints of the fibril structure, or elevated surfaces areas were obtained from these early attempts.[39,96,156,264–270] A first successful hierarchical wood replication was reported by Shin et al.[271] This work omitted the selective lignin removal step but used surfactants to ease cell wall accessibility. This work

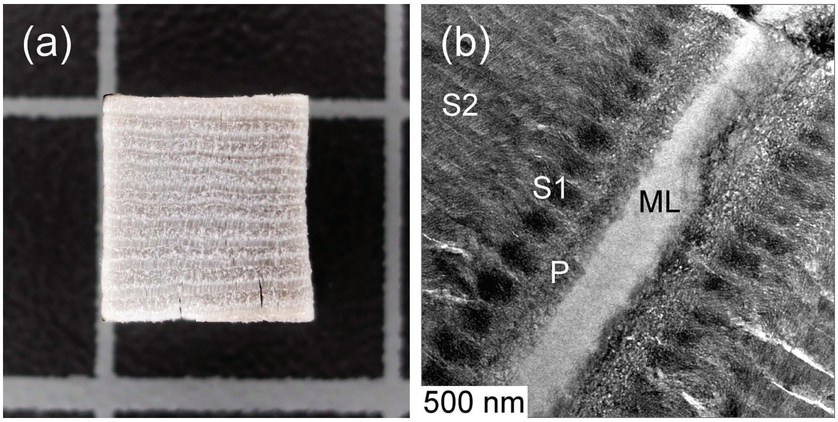

Figure 10. a) Photograph and b) transmission electron micrograph of replicated silica from wood, showing the replication of the outer shape including the early- and latewood cellular structure as well as the intricate nanometer cell wall structuring with retained former (ML) middle lamella, (P) primary, (S1, S2) secondary cell wall layers. The cracks are preparation artifacts.

could however not conclusively demonstrate the nanofibrillar level replication of the wood structure. By using Kraft-pulp as the template and untreated wood as the control, it could be shown in[50] that the preparation of biotemplated silica with fibrillar structuring on the nanometer scale and high specific surface areas requires an equally nanoporous template. The first work to use wood samples and a selective lignin removal, which were followed by cerium/zirconium oxide nanoparticle infiltration, led to the successful replication of the entire hierarchical wood structure.[51] This was demonstrated by small-angle X-ray scattering, which had previously been used to determine the cellulose fibril arrangements in wood cell walls.[194,272,273] Scattering patterns from replicated and calcined wood samples with different microfibril angles clearly demonstrated the fibrillar level replication, while maintaining the entire hierarchy up to macroscopic dimensions. It could however not be proven, whether the level of the cellulose elementary fibrils was replicated as well, Figure 7c.

The method employed in ref. [51] was recently adapted to silica replication of wood, and refined by adding a maleic acid anhydride treatment step and infiltration with TEOS in ethanol, thereby producing detailed and stable silica replicas of the entire wood structure,[54] **Figure 10**. In situ small-angle X-ray scattering during calcination was used to follow the structure evolution of the infiltrated material in TEOS infiltrated wood.[250] This work clearly demonstrated that for delignified (and optionally functionalized) wood, the cellulose nanofibrils of only about 2–4 nm in diameter were transformed into pores of approximately the same diameter, thus confirming the replication of the lowest hierarchical level in wood. This work also suggests that the molecular precursor probably enters the fibrils (Figure 7c) via the swellable hemicelluloses, building a hemicellulose/silica matrix with embedded cellulose nanofibrils. During the template removal, the hemicelluloses decomposed first, at temperatures around 300 °C, followed by cellulose nanofibril decomposition at around 400 °C and leading to parallel helical pores in the resulting ceramics, **Figure 11**. In combination with the cellular porosity on the micrometer scale, the resulting material showed a hierarchical porosity with roughly cylindrical structures at the micrometer level (20–40 μm), and helical porosity at the level of the microfibrils (10–20 nm) and the elementary fibrils (2–4 nm).[250]

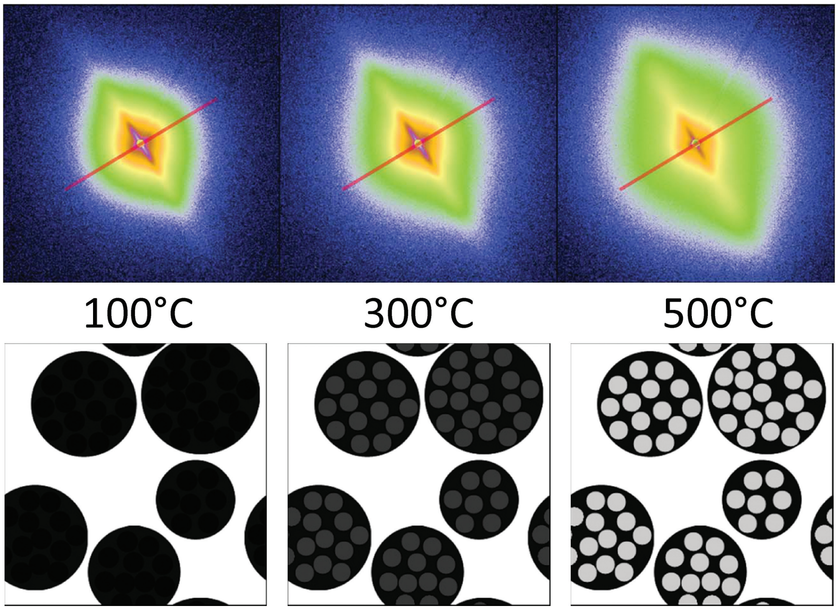

Figure 11. Small-angle X-ray scattering patterns (top) and structural model fitted to the data (bottom) of wood-inorganic composite after infiltration (left) and resulting silica replica (right) with an intermediate state (middle). The diameter of the small circles (nanofibrils) is 2.7 nm and the size of the large circles (fibrils) is 12.6 nm. The fibril orientation is observable from the anisotropy of the scattering pattern (red line). After infiltration and drying, cellulose nanofibrils in a silica/hemicellulose matrix with very similar electron density cause the "invisibility" of the nanofibrils. At increased temperatures, the scattering intensity at higher angles increases, caused by the replacement of the cellulose nanofibrils by pores, which are now "visible" due to their different electron density as compared to silica. Adapted with permission.[250] Copyright 2012, Wiley-VCH.

A common property of the wood replicas is their high surface area,[50,51] which might be useful for functional applications such as separation or catalysis. Biotemplating by delignification of pine wood, maleic acid anhydride treatment and repeated infiltration with ethanolic solutions of tetraethyl orthosilicate followed by calcination at 500 °C leads to materials with surface areas beyond 500 m^2/g. It should however be noted that for higher calcination temperatures the surface area becomes lower and the entire nanostructure collapses within a short time interval if the temperature exceeds 900 °C.[250]

5.3. Nanoscale Replication of Other Plant Structures

The principles of nanometer-precision replication of wood can be directly transferred to other plant materials such as the peel of the pomelo fruit.[77] The resulting silica replica had micrometer-sized gradient pores, perfectly replicating the pomelo peel cell structures and nanometer sized pores resulting from the cell wall fibrillar structures. This makes the resulting material a multiscale hierarchical material, of which one scale in turn contains a structure size gradient (see Figure 1). The extremely complex gradient structures at the micrometer scale are known to be optimized with respect to the uptake of large amounts of energy without breaking. Similar bioinspired gradient materials have also been produced using elaborate manufacturing techniques,[85] currently however covering only one hierarchical level.

By applying similar biotemplating principles, green leaves were used to prepare hierarchically structured titania with improved photocatalytic activities.[261] This was based on the detailed replication of the stacked thylakoid membranes within the chloroplasts, the grana. A template preparation by ion exchange and water removal followed by an alkoxide precursor infiltration and template removal at 500 °C led to a hierarchical structuring detail with 10–15 nm thick titania layers. Notably, this work produced nanocrystalline materials similar to the cerium/zirconium oxide templated wood described above.[51] This demonstrates that also crystalline phases may be derived, although for nanoscale replicas the crystallites must remain small. Fast crystallization with associated large and abrupt volume changes as well as crystal growth beyond the nanometer scale will lead to the collapse of nanostructural features. Consequently, high temperatures and high crystallization pressures will remain a problem concerning biotemplating of the nanometer scale.

6. Conclusion and Outlook

The transformation of structural elements or - in ideal cases - the entire structural hierarchy of biological tissues is still a challenging, yet worthwhile synthesis strategy for advanced functional materials. Recent research of our groups and others demonstrated that the replication detail of biological templates can be extended to the nanometer scale by adhering to certain specific processing steps. These were reviewed with focus on the prominent examples of lignocellulosic substances, and in particular wood. The template preparation typically includes a selective component removal step to create open spaces into which the inorganic precursor can be infiltrated. After optional chemical functionalization, an infiltration step is followed by a sol-gel condensation reaction and template removal by thermal oxidation, condensing the infiltrated material and gradually removing the biotemplate. The choice of the target material is dependent on the crystallization behavior of the material, which must result in an amorphous or nanocrystalline phases after thermal template removal. The resulting inorganic porous materials are characterized by multiscale hierarchical structures with high surface areas. They may be promising materials for advanced applications such as chirally selective adsorbing materials for separation columns, structurally enhanced (photo) catalysts, gas sensors, or mechanical applications, including actuation. The feasibility of such functional applications is the subject of intense current research in many groups and may necessitate the further processing of the replica such as the inclusion of a second phase into the nanometer-sized pores.

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