Nanostructures

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# Biopolymers as a Flexible Resource for Nanochemistry

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***B**iomass is an abundant source of chemically diverse macromolecules, including polysaccharides, polypeptides, and polyaromatics. Many of these biological polymers (biopolymers) are highly evolved for specific functions through optimized chain length, functionalization, and monomer sequence. As biopolymers are a chemical resource, much current effort is focused on the breakdown of these molecules into fuels or platform chemicals. However there is growing interest in using biopolymers directly to create functional materials. This Minireview uses recent examples to show how biopolymers are providing new directions in the synthesis of nanostructured materials.*

## 1. Introduction

From cellular information storage to protective shells, living organisms produce macromolecules with an extraordinary range of functions.[1] The most abundant macromolecules are the structural polymers, which provide support and protection in the form of cell walls, scaffolds, or tough exoskeletons. Structural polymers encompass diverse chemistries: amide-, carboxylate-, or sulfate-functionalized polysaccharides as well as polypeptides and polyaromatics. Many structural polymers exist as ordered composites with proteins, other polymers (e.g. lignocellulose), and/or inorganic materials.[2] Cellulose molecules in plants, for example, are aggregated through strong hydrogen bonds into crystalline fibrils (Figure 1 A). These assemble into fibers, separated by amorphous material, and provide strength and flexibility to the plant. Collagen molecules in animal tissues form similar fibers that give for example, tensile strength as part of a composite with hydroxyapatite in bone.[3] In many organisms, the biopolymer fibers are ordered into complex, long-range patterns with multidirectional mechanical strength, such as the helical Bouligand or "plywood" structure of chitin in crustacean shells (Figure 1 B).[4] In addition to these fibrillar polysaccharides and polypeptides, the biopolymers that exist in the interfibrillar and intercellular regions (e.g. alginate in algae) can also play a key role in structural integrity as well as having other functions, such as ion exchange.[5] Alternatively, some polysaccharides are secreted by bacteria as protective or adhesive coatings, such as dextran or xanthan gum.

Various chemical processing techniques have been devised to disassemble biomass and isolate the constituent biopolymers. In some cases, the aim is to maintain the natural anisotropic structures.[6] This is used extensively with cellulose, by applying, for example, acid treatment to cleave the amorphous regions. The resulting microfibrils and nanocrystals have been applied widely in reinforced polymers, aerogels, or as templates, and several reviews exist on this work.[7] Most methods, however, focus on chemical extraction to produce a water-soluble biopolymer, often by acid or alkaline hydrolysis. In many cases the extracted polymer is chemically distinct from the source (e.g. chitosan is the deacetylated form of chitin), and biopolymers can have very different properties depending on the extraction method. A particularly good example of this dependence on the extraction is gelatin, the gel strength and isoelectric point of which are determined by the pH value and temperature during the extraction. Some biopolymers are precipitated as salts (e.g. Na/K/Ca alginate) after extraction, and the properties can depend on the nature of the counterion. Finally, derivatization is used widely to tune physical properties and solution

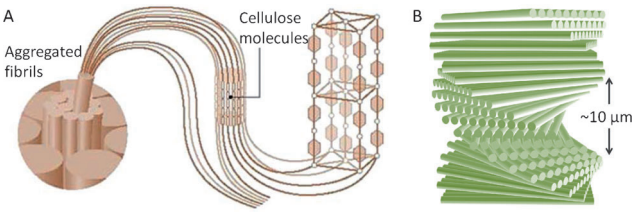


***Figure 1.*** A) Schematic of crystalline packing of cellulose in plants and B) twisted plywood stacking of chitin fibrils in crustaceans. Figures adapted with permission from references [7b] and [4], respectively.

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behavior of biopolymers. For example, cellulose is swelled in alkali to disrupt the crystalline regions and then can be substituted at the hydroxy groups by reaction with, for example, sodium chloroacetate. The properties of the resulting carboxymethylcellulose depend strongly on the degree of substitution.[8] Some examples of key biopolymer sources, structures, extractions, and properties are listed in Table 1.

Perhaps the most intriguing feature of biopolymers is their specialization. Unlike the statistical distributions common to many synthetic polymers, biopolymers often have well-defined chain lengths, monomer sequences, and stereochemistry. The complex primary, secondary, and tertiary structures of proteins are well-known, but even within the seemingly simple polysaccharides there can be sequences and assemblies evolved for specific functions. Many of the extracted structural polysaccharides and polypeptides form single, double, or triple helices in water through hydrogen bonding or in some cases ionic crosslinking. Some of these structural polymers form extended hierarchical networks, trapping water in a gel (Figure 2). These gels can be thermoreversible, with the

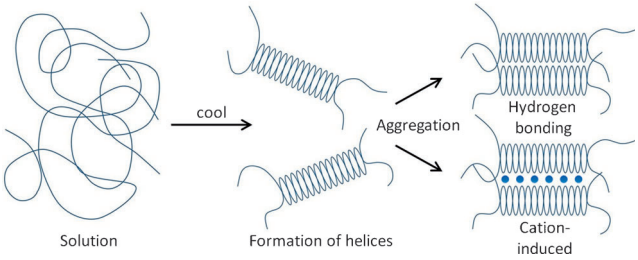



***Figure 2.*** Gel formation through aggregation of helices.

polymers returning to random coils on heating (gelatin, agar) or dependent on pH value (chitosan, alginate) or the presence of metal ions (alginate, pectin, carrageenan). Some polymers have limited solubility in water but exhibit swelling in hot water (alginic acid and some starches depending on the amylose/amylopectin ratio). As with many biological systems, structure depends on required function, and the properties of a particular biopolymer can vary considerably between species, within different parts of a living organism, or depending on growth conditions such as climate. Perhaps the most interesting example of this variability is alginate, one of the main structural polymers of marine algae. Alginate is a copolymer of α-(1-4)-guluronate (G) and β-(1-4)-mannuronate (M) consisting of homopolymeric (GGGGGG, MMMMMM) and alternating (GMGMGM) blocks. The composition and G/M ratio depend on both the source species and the location within the plant. Blocks of guluronate are strongly crosslinked by multivalent metal cations to give microcrystalline regions in a mechanism known as the "egg-box" model (Figure 3), and it is through this variation of cation binding with sequestration of divalent cations from seawater that many seaweeds tailor their mechanical strength.[9]

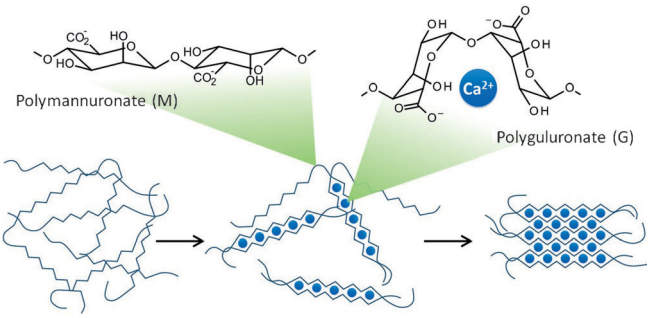



***Figure 3.*** The egg-box model of cation binding in alginates.

As a resource for nanochemistry, biopolymers have many advantages. They are naturally abundant and many are extracted industrially on a large scale[10] or are low-value waste products, for example, lignin from kraft pulping. They are chemically and structurally diverse and the properties can vary considerably depending on the source and method of extraction. While the extraction requires careful monitoring to ensure homogeneity, the variations in the method and the source offer extensive tunability of the properties of the biopolymers. In foods, cosmetics, and pharmaceuticals, these subtle variations are used widely, for example to optimize rheological properties. In materials chemistry, however, this potential is only now being realized. The aim of this Minireview is to showcase the broad spectrum of possibilities for biopolymers in nanostructure synthesis, including several emerging applications. Some examples rely on the structure, functionality, and supramolecular arrays of biopolymers to direct assembly or growth. The biopolymers can be sacrificial or become an integral part of the product as a composite.[11] Alternatively, the entire product can be synthesized purely from the biomaterial, as in the synthesis of functional porous carbon materials. Many of the examples involve inorganic materials, but there are also cases where biopolymers are used to modify the structure of "soft" materials such as polymers. Both extracted biopolymers and native biomass will be considered, with a particular focus on the specific advantages of the biomaterial in each case. It would be impossible to cover the full range of biopolymers and so this Minireview focuses on some of the most abundant and readily available varieties. The term 'biopolymer' is sometimes used to describe polymers that have been synthesized from bio-derived monomers, for example, poly(lactic acid). However, this Minireview will only consider macromolecules that are produced directly by living organisms.

*Zoe Schnepp completed a Ph.D. with Prof. S. Mann FRS at the University of Bristol, UK. After a postdoctoral fellowship at the Max Planck Institute for Colloids and Interfaces, she joined the International Center for Young Scientists at the National Institute for Materials Science, Japan. Recently she was appointed as a Birmingham Fellow in the University of Birmingham, UK. Her research interests are green chemistry routes to nanomaterials.*

***Table 1:*** Summary of some key classes of biopolymers with common examples.

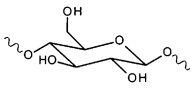
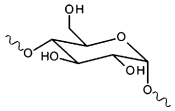
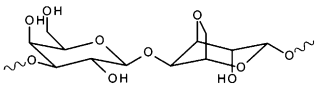
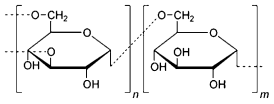
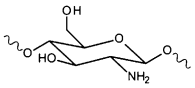
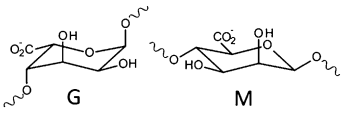
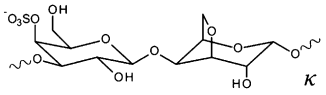
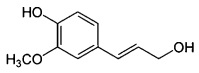
| Category | Example | Primary source | Typical monomer | Key properties |
|---|---|---|---|---|
| neutral polysaccharides | cellulose | structural biopolymer in plants, also produced by some bacteria |  | -linear polymer, most abundant naturally occurring polymer<br>-insoluble in water and many solvents; alternative solvents include ionic liquids, DMAc/LiCl, NMMO[a]<br>-nanocrystals can be extracted by e.g. acid treatment<br>-derivatization increases hydrophilicity, e.g. carboxymethylcellulose |
| | starch | energy storage polymer in higher plants |  | -mixture of homopolymers of α-D-glucose: amylose (linear) and amylopectin (branched), depending on source<br>-crystalline and amorphous regions<br>-hydrophilicity depends on content<br>-many functional derivatives available e.g. crosslinked, acetylated, partially hydrolyzed |
| | agarose (agar) | acid or alkaline extraction from rhodophyceae (red algae) |  | -linear alternating copolymer, dissolves in boiling water to give random coils<br>-cools to strong thermoreversible gels through formation of left-handed double helices, which aggregate through intermolecular hydrogen bonding into larger fibrillar networks |
| | dextran | enzymatic fermentation of sucrose by bateria (e.g. *Leuconstoc* Mesentreroides) |  | -branched glucan<br>-composition typically 95% 1,6-linkages and 5% randomly distributed 1,3-linkages<br>-very high solubility in water, low viscosity and compatible with acid/base/salts<br>-wide range of molecular weights<br>-dextran sulfate also available commercially, with stronger metal binding |
| cationic polysaccharides | chitosan (chitin) | base-catalyzed deacetylation of chitin from arthropod shells |  | -most abundant polysaccharide on earth after cellulose<br>-properties of chitosan depend on degree of deacetylation (DD)<br>-chitin has limited solublility (e.g. ionic liquids, DMAc/LiCl, $CaCl_2$/methanol)<br>-chitosan dissolves in dilute acetic acid and binds to transition metal ions<br>-many functionalizations available |
| anionic polysaccharides | alginate | hot alkaline extraction from brown algae (phaeophyceae) |  | -linear block copolymer of two epimers guluronate and mannuronate (GGGGGG, MMMMMM, GMGMGM)<br>-G/M ratio depends on source (ca. 40–75% G)<br>-alginic acid insoluble in water; $Na^+/K^+/NH_4^+$ salts soluble<br>-crosslinked by multivalent metal cations |
| | carrageenan | hot alkaline extraction from rhodophyceae (red algae) |  | -linear polymers<br>-κ- and ι-carrageenans form thermoreversible rigid (κ-) or elastic (ι-) gels in water through coil–double helix transformation, then metal cation induced aggregation (e.g. $Ca^{2+}$) to form junction zones<br>-λ-carrageenan is soluble in hot water but nongelling |

*Table 1:* (Continued)

| Category | Example | Primary source | Typical monomer | Key properties |
|---|---|---|---|---|
| polypeptides | gelatin | acid or base conversion of collagen, major structural protein in animal tissue | -Gly-Pro-Arg-Gly-Glu-4Hyp-Gly-Pro- | -most abundant protein in animal kingdom<br>-chemistry depends on extraction method<br>-peptide sequence and chain length depend on source but normally 1/3 glycine<br>-thermoreversible gels in water—strength depends on gelatin type<br>-soluble in some alcohols |
| polyphenol | lignin | structural component of plants |  | -complex 3D heteropolymer, hydrophobic<br>-sulfite pulping gives water-soluble lignosulfonate<br>-major byproduct of paper and pulp industry |

[a] DMAc = *N*,*N*-dimethylacetamide, NMMO = *N*-methylmorpholine-*N*-oxide.

## 2. Biomimetic Nanostructure Synthesis

Many organisms use functional organic biopolymers to aid sequestration of metal species from their environment and direct mineralization of an inorganic phase.[12] Both soluble components and solid frameworks can influence morphology and in some cases crystal polymorph by adsorbing preferentially to certain crystal faces or providing a constraining matrix for mineralization.[13] In vitro, these effects can be mimicked either to probe the mechanism of biomineralization or to produce complex and functional inorganic nanostructures.[14]

### 2.1. Directed Growth with Soluble Biopolymers

Soluble polymer additives offer a high level of control in both classical and nonclassical crystallization, since the multiple functional groups can allow stronger binding than low-molar-mass counterparts. These additives can influence crystal growth through surface-specific adsorption to crystal faces, or steric and electrostatic stabilization of nanoparticles either to prevent or control aggregation. Certainly, there are many examples of morphosynthesis using specialized macromolecules extracted from mineralized biological systems, such as mollusc shells[15] or sponge spicules.[16] However, perhaps the most extensive application of this chemistry is the use of simple polysaccharides for controlled growth of coated nanoparticles, for example, dextran/$Fe_3O_4$,[17] starch/Ag[18] and Au[19], or gelatin/poly(acrylic acid).[20] Here, the large number of hydroxy groups on the biopolymer enables specific binding to precursor cations or monomers and thus formation of small nanoparticles.[21] This same functionality can then bind the polymer strongly to the nanoparticle surface, particularly in the case of metal oxides. Additionally, hydrophilic biopolymers such as alginate or gelatin can be used to stabilize nanoparticle colloids of hydrophobic materials such as carotene.[22] Of course, many synthetic polymers can also perform these functions. However, polysaccharides such as dextran or chitosan combine this templating effect with excellent biocompatibility and biodegradability, which is advantageous, for example in medical applications.[23] Furthermore, many polysaccharides are also available in a wide range of molecular weights, which can be used to control particle size. A final specific advantage is that there are often very specific enzymes available to break down biopolymers. These enzymes can be used to "deshell" the coated nanoparticles, potentially to tune hydrodynamic radius or deliver active trapped molecules.[24]

### 2.2. Directed Growth in Biopolymer Gels

Long-range order and complexity in biominerals is often directed by a hierarchical biopolymer scaffold. This extended organization typically arises from intra- and intermolecular hydrogen bonding and (in some cases) ionic crosslinking of biopolymers with metal cations. Many extracted biopolymers self-assemble into helices in water through similar interactions and some form extended networks that trap water in a gel. Growth of materials within the gel network is then greatly affected by reduced diffusion rates, compared to bulk solution where convective transport is dominant.[25] Again, this concept has also been demonstrated in synthetic polymer gels, but biopolymer gels offer many advantages. Biopolymer gels are often very responsive to changes in temperature (e.g. gelatin, agar), pH value (e.g. chitosan), or the presence of metal cations (e.g. alginate, pectin), and there is a lot of scope for using this responsiveness in the preparation of useful materials.

In general, there are several distinct approaches to synthesizing materials in biopolymer gels, as outlined in Figure 4. The first approach normally involves addition of soluble ionic or molecular precursors to the biopolymer and then inducing gelation by, for example, cooling or changing the pH value.[26] The precursors are stabilized within the gel through complexing or hydrogen bonding to the biopolymer. As in the previous section, this stabilization of precursors can be used for controlled nucleation and growth of nanoparticles through, for example, heating, addition of a reducing agent, or inducing a pH change (Figure 4 A). In this case, however, the fibrous gel network can be used to align the resulting nanoparticles to form, for example, linear arrays of gold nanoparticles with an associated blue shift in the plasmon band.[27] The natural variability of biopolymers, for example, the G/M ratio in alginate, can also be used with this method to

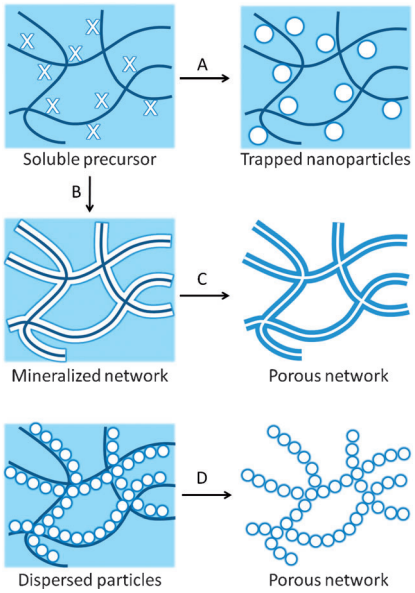



***Figure 4.*** A) Precipitation of nanoparticles from aqueous precursors or B) mineralization of the gel network and C) removal of the organic gel by for example, calcination. D) Use of a gel network to assemble presynthesized nanoparticles before sintering into a porous network.

control nanoparticle size[28] or even crystalline phase[29] through associated changes in metal binding strength. Similarly, ι-, λ-, and κ-carrageenan have been shown to have a strong effect on magnetite particle size from coprecipitation, owing to differences in sulfate functionality, metal binding strength, and physical properties (and thus diffusion rates in the gel).[30] In some cases, the biopolymer is then removed. However, nanoparticle–biopolymer composites prepared using these and similar methods are finding increasing interest as catalyst/support combinations for fine chemical synthesis.[31] In this case, careful removal of water (e.g. freeze drying) can maintain the high porosity of the biopolymer gel in a sponge-like product.

By using various metal-containing precursors, aqueous biopolymer gels can be mineralized (Figure 4B) to form fibrous metal oxide–biopolymer composites or aerogels by removing the organic matrix (Figure 4C).[32] There are many examples for silica, and in this case, the hydroxy groups common to many biopolymers have been shown to accelerate and direct condensation of the silica network through hydrogen bonding with silanol groups.[33] Likewise, binding of the silica precursor can promote gel formation in nongelling biopolymer systems.[34] One disadvantage of this method is that many metal oxide precursors hydrolyze rapidly with water, and so an alternative approach is to exchange the solvent in the biopolymer gel before infiltration of, for example, a metal alkoxide precursor.[35] The structure and properties of gel-templated inorganic materials were shown to depend on polysaccharide type, charge, and concentration and could also be varied through biopolymer source, for example, ι-, λ-, and κ-carrageenan. It should be noted that the silica-mineralization method can actually be used to enhance accessibility of the biopolymer functional groups (e.g. -NH in chitosan) for applications in catalysis through formation of the hybrid aerogel.[36] Interestingly, the weaker hydrogen-bonding interactions of biopolymers with molecular precursors can also be used to direct polymerization of fibrous structures of, for example, polypyrrole[37] or polyaniline.[38] As an alternative to ionic or molecular precursors, biopolymer gels can be used to disperse and organize presynthesized nanoparticles (Figure 4D) before sintering to produce porous monoliths of, for example, hydroxyapatite,[39] $TiO_2$,[40] zeolites,[41] or carbon nanotubes.[42]

### 2.3. Higher-Order Nanostructuring

The complex intermolecular interactions and structures exhibited by many biopolymers can be used to prepare nanomaterials with long-range ordering or anisotropic structure. DNA and tobacco mosaic virus are well-known templates for anisotropic structures, but there are also examples that use simple polysaccharides. These examples generally rely on the ability of many polysaccharides to form single, double, or triple helices in water, often with a hydrophobic core. The helices can be used as 1-dimensional supramolecular hosts for, for example, "wrapping" of carbon nanotubes,[43] aligning gold or silica nanoparticles,[44] assembling polyaniline strands or organic dye molecules,[45] or templating silica nanowire formation.[46] A particular advantage is that the cavity size of polysaccharide helices is often quite flexible, depending on the host. Furthermore, the inherent chirality of helices can also be used to induce chirality into the product, for example, through encapsulating oligosilane in left-handed amylose (Figure 5) or right-handed schizophyllan.[47] Alternatively, the chirality of a polysaccharide has been shown to selectively produce one polymerization product from a mixture of ethers.[48] A different approach uses single biopolymer strands as templates for 1D hollow structures. For example, Greil and co-workers functionalized cellulose with oligopropylamino groups, which are key components of natural biosilica proteins such as silaffins. The cellulose then acted as a stiff backbone for the amino sites, which directed regioselective polycondensation of tetraethoxysilane into hollow silica nanotubes.[49] On a larger scale, the native crystalline structures of some biomass can be used as templates. For example, microfibrous cellulose, produced from pulping, is composed of bundles of interconnected nanofibers that consist of highly ordered crystalline domains

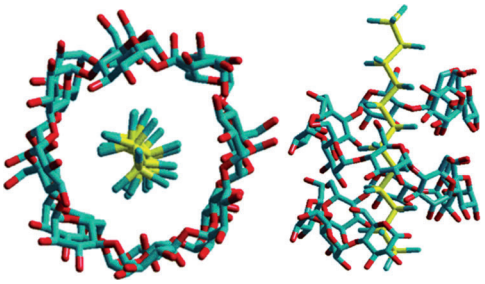


***Figure 5.*** Amylose helix directing chirality of oligosilane; C green, O red, Si yellow (adapted with permission from reference [47]).

of cellulose alternating with disordered, amorphous regions. These fibrous structures are used widely in composite materials,[50] often for structural reinforcement. Acid hydrolysis of cellulosic biomass leads to dissolution of the disordered regions, thereby leaving rod-like crystalline cellulose nanofibers bearing anionic sulfate ester terminating groups. These nanofibers have been used widely as templates, for example, to align metal or semiconductor nanoparticles.[51] Another feature of the nanocrystalline cellulose is that the particles organize into a chiral nematic phase, which can be mineralized to produce a mesoporous birefringent silica with long-range chiral ordering.[52] Similar structures have been prepared using arrays of collagen fibrils.[53]

#### 2.4. Biopolymer Films to Direct Structure and Polymorph

In living organisms, mineralization often takes place within a structured environment, for example, lipid vesicles or organized collagen network. This environment effectively acts as a mould and allows the organism to control the composition and concentration of the precipitation solution. While we have already discussed the effectiveness of biopolymer gel networks for influencing nanostructure growth, there is also a lot of important work using biopolymer surfaces to influence morphology and polymorph of thin films in conjunction with soluble additives.[54] Much of this research has focused on $CaCO_3$, by using solid biopolymer substrates such as chitin, chitosan, or cellulose in conjunction with soluble poly(acrylic acid) to grow thin films of either vaterite or calcite, depending on the chemical functionality of the biopolymer.[55] The film growth is thought to occur through binding of the poly(acrylic acid) to -OH and -NH groups on the biopolymer surface and subsequent sequestering of $Ca^{2+}$ ions to induce mineralization. By using a mineralizing protein extracted from crayfish shells as the soluble component, this templating effect can be extended to produce orientated crystals.[56] Alternatively, a cholesterol-functionalized polysaccharide was used as a "soft" hydrogel surface, inducing patterning in the resulting $CaCO_3$ film, presumably through the influence of surface diffusion effects.[57]

## 3. Sol–Gel-Type Routes

The examples in this section could be classed as a form of templating or directed growth, since the key emphasis is still on controlled crystallization. However, it is mechanistically more instructive to consider these sol–gel-type routes separately, since they involve ceramic materials, which may pass through several crystalline intermediates and/or where growth of the final product occurs well above the decomposition temperature of the polymer.

#### 3.1. Biopolymer Sol–Gel for Metal Oxides

Traditional sol–gel chemistry involves hydrolysis and condensation of metal alkoxides ($M(OR)_x$) to form metal-oxane networks. The structure of the gel depends strongly on the relative rates of these two reaction steps, which can be controlled by factors such as pH value, chemical nature of the alkoxide or stabilizing ligands. For many metals, however, the hydrolysis of alkoxides is too fast for traditional sol–gel chemistry to be possible. One alternative is to create a dispersion of aqueous metal cations by using chelators, such as citrate, which lower the equilibrium constant for hydrolysis of the metal. Thus evaporation of solvent results in a homogeneous "glassy" state with intermolecular hydrogen bonding, rather than uncontrolled precipitation of metal hydroxide particles. Heating this precursor then initiates nucleation and growth of metal oxide crystallites, along with combustion of the organic species.[58] Compared to traditional solid-state synthesis of ceramics from mixed powders, the "gel" precursor generally leads to much smaller particle sizes and lower synthesis temperatures. Further stabilization of the initial "gel" state can be achieved by in situ polyesterification of citrate with ethylene glycol, the so-called "Pechini method".[59] The interpenetrating covalent network can maintain homogeneity to a much higher temperature than a simple dispersion of chelate complexes. This polyesterification method provides greater control over nucleation and growth of crystallites and is particularly effective for synthesizing ternary or quaternary metal oxides with precise cation stoichiometry. Alternatively, the metal cations can be dispersed in a polymer network, for example, poly(vinyl alcohol) or poly(acrylic acid). This method is sometimes referred to as the "polymer complex method".

Biopolymers are particularly attractive for the "polymer complex method" owing to their ability to form a strong gel with metal cations. Thus, heating a biopolymer/metal salt gel in air leads to constrained nucleation of metal oxide crystallites. Simultaneous decomposition of the organic matrix prevents grain growth and typically results in a sponge-like network of nanoparticles, for example, CuO,[60] $WO_3$,[61] or $YBa_2Cu_3O_{7-x}$.[62] This method can be combined with in situ reduction of metal ions by the aldehyde or carboxylate groups of dextran or alginate, respectively to produce nanostructures of, for example, $Au/CeO_2$[63] (Figure 6A). Alternatively, controlled precipitation of intermediate metal hydroxide particles can be carried out by increasing the pH value within the biopolymer gel before calcination to produce the metal oxide.[64] Notably, controlled gelation of the biopolymer can be used to produce materials with nano- and macroscale features by, for example, dropping or extruding alginate into a metal salt solution to produce spheres or fibers.[65]

The ability of biopolymers such as alginate to 'organize' metal cations into gels with regions of short-range order has allowed unprecedented control of morphology in the sol–gel-type synthesis of metal oxides.[66] Indeed, biopolymers were able to produce anisotropic structures of quaternary metal oxides, which were previously thought to be unobtainable by solution routes.[67] In this case, the biopolymer controls morphology of the final ceramic product by directing nucleation, growth, and distribution of intermediate crystalline phases. Specifically, the formation of $YBa_2Cu_4O_8$ nanowires from sodium alginate and aqueous acetates was shown

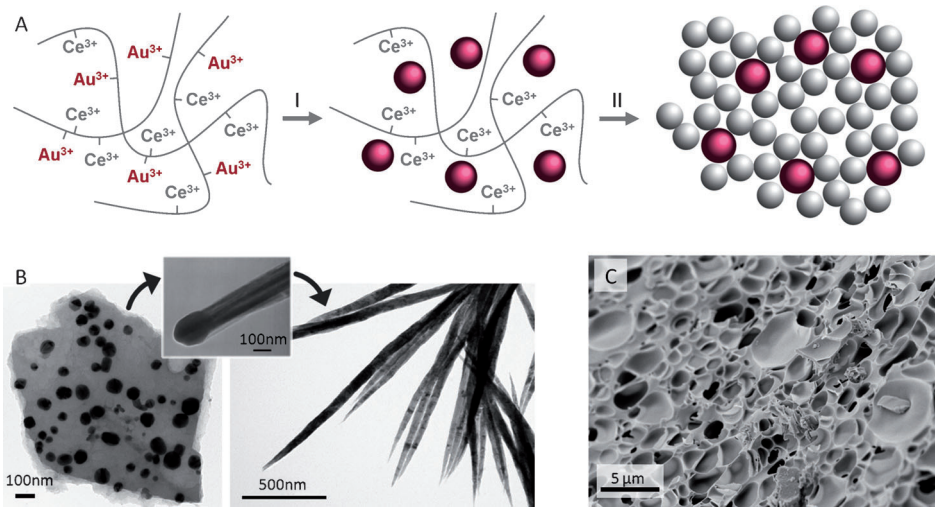



***Figure 6.*** A) One-pot synthesis of an $Au/CeO_2$ nanocomposite from alginate gel containing $Ce(NO_3)_3$ and $HAuCl_4$ includes (I) initial controlled nucleation of Au nanoparticles with gentle heating, then (II) calcination and controlled nucleation of $CeO_2$ nanoparticles. B) $YBa_2Cu_4O_8$ nanowires from alginate through solution-liquid-solid (SLS) growth from $BaCO_3$ nanoparticles. C) Iron nitride nanoparticle sponge prepared from gelatin. Figure adapted with permission from references [63, 68], and [70c], respectively.

to proceed via nanoparticles of $BaCO_3$ embedded in a matrix of amorphous or poorly crystalline Y, Cu, and Na salts (Figure 6B).[68] On melting, these droplets are believed to act as catalysts for solid-liquid-solid outgrowth of the $YBa_2Cu_4O_8$ nanowires. Notably, a high guluronate content (and thus strong organization of metal cations) was shown to be crucial for nanowire formation. Recently, this method has been extended to the soft templating of 'soft' materials in the controlled crystallization of a metal-free semiconductor, graphitic carbon nitride (g-$C_3N_4$).[69] In this case, the homogeneous precursor gel comprised of dicyandiamide dispersed through hydrogen bonding with either gelatin or alginate. During polymerization to g-$C_3N_4$ at 500 °C the biopolymer acts as a porogen, generating a final material with enhanced surface area and consequently a higher photoactivity. There are few examples of this type of soft templating of soft materials—most techniques to increase porosity rely on hard templating with, for example, silica spheres, which then require etching with HF or NaOH—and so the in situ combustible biotemplate opens many new possibilities.

### 3.2. Dual-Function Biopolymers for Metal Carbides, Nitrides, or Hybrid Nanocomposites

Heating a metal–biopolymer gel in an inert atmosphere ($Ar/N_2$) can be used for the controlled synthesis of transition metal carbide and nitride nanostructures, such as $Fe_3C$ and $Fe_3N$ (Figure 6C),[70] or metal–carbon nanostructures. As with the above examples, the first step is constrained nucleation of nanoparticles of a metal oxide intermediate. In this case, however, the biopolymer simultaneously decomposes to form a carbon-rich matrix, which on further heating causes carbothermal reduction or nitridation of the oxide nanoparticles. A particular advantage of these routes to metal nitrides is that nitrogen is sourced directly from the biopolymer, thereby removing the need for traditional but hazardous ammonolysis. Again, there are many other synthetic polymers or indeed small molecules that can achieve the same sol–gel-type synthesis of carbides or nitrides. However, the interesting physical properties of many biopolymers can be exploited in this case to introduce structural complexity into the product. For example, gelatin/metal nitrate hydrogels often foam on drying to produce expanded sponge-like structures. This property can be exploited to produce a metal carbide/nitride with high accessible porosity. Most recently, biopolymers have been used to produce hybrid oxide/nitride or oxide/carbide nanocomposites (e.g. $TiO_2/Fe_3C$) in a one-step sol–gel-type process.[71] This process relies on the different stability of oxide intermediates to achieve selective carbothermal reduction or nitridation. The homogeneous biopolymer precursor ensures that the two oxide intermediates are highly interdispersed, thus leading to a composite with very small particle size ($< 10$ nm).

## 4. Biotemplating with Native Biomass

Nature has evolved structures that are optimized to specific functions, for example, the porous tubular arrays in wood that offer strength and flexibility while simultaneously providing a route for water and nutrient transport through the tree. Many of these natural structures display complex ordering of biopolymers, such as the microfibrillar composite of cellulose and lignin in the cell walls of woody plant matter. By templating the biomaterial we can harness this structural complexity, either to mimic a natural function such as a photonic crystal[72] or for an entirely new purpose, for example, catalysis. Templating is used widely, not only with biomaterials, and there are many reviews of the field.[73] The term "templating" encompasses diverse techniques, and this section will focus on hard templating of native organic

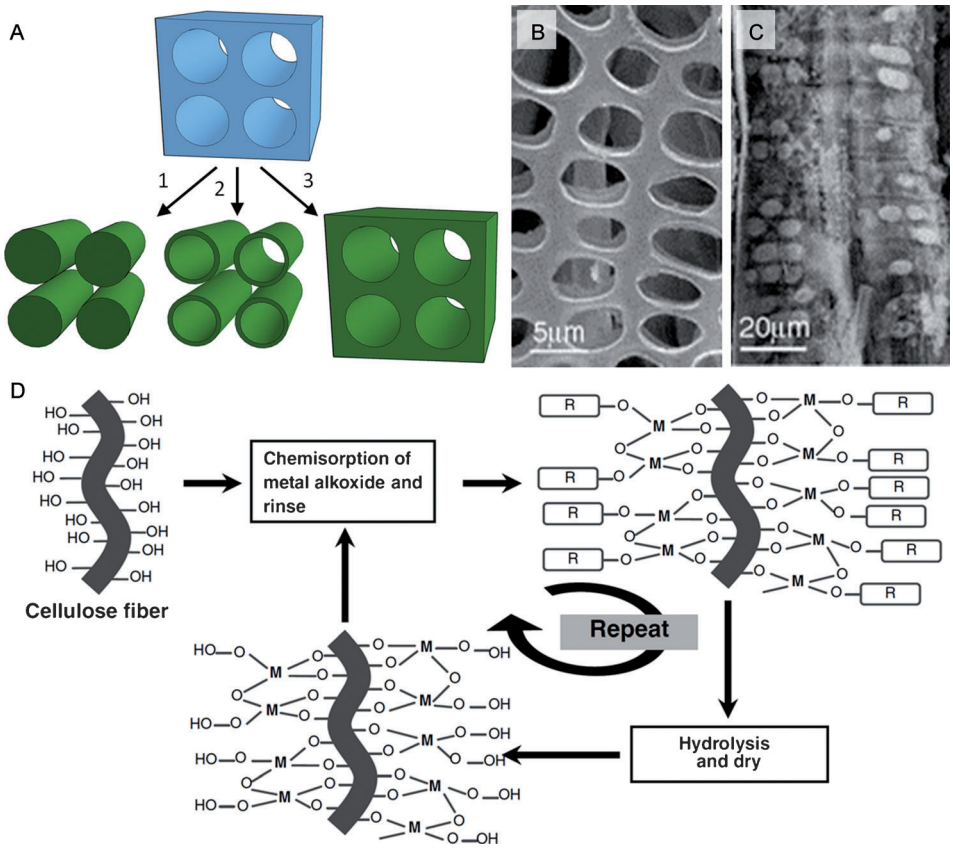



***Figure 7.*** A) Schematic of the different methods of templating to produce 1) negative and 2) positive copies and 3) direct replicas. B, C) Examples of a replica (B) and an inverse of poplar wood (C) from slow and fast hydrolysis of silica precursors; with permission from reference [75]. D) Schematic of sequential chemisorption and hydrolysis to build atomic-size layers of metal oxides on a template surface; with permission from reference [76b].

biomass to produce negative (inverse) and positive (hollow) copies or direct replicas (Figure 7A).

### *4.1. Optimizing Biomass for Templating*

A wide range of organic biomaterials, including wood, paper, cotton, or fungi, have been used to template ceramic materials.[74] This templating is often achieved by infiltration of the biomaterial with inorganic precursors and precipitation of an amorphous, polycrystalline, or more rarely a single-crystal ceramic product. The template could essentially be seen as a cast, providing a confined space for mineralization. However, the choice of conditions and also of the inorganic precursor can have a dramatic effect on the resulting material. For example, templating poplar wood with sol–gel silica precursors under conditions of slow hydrolysis and condensation produced a fine-structured replica, since the precursors were able to leach into the cell walls (Figure 7B).[75] Fast hydrolysis, on the other hand, produced a simple inverse structure (Figure 7C). An advantage of many organic biomaterials for templating is that they often exhibit functional surfaces owing to the biopolymer content. These can be exploited to achieve accurate templating through surface-specific chemisorption of, for example, metal alkoxides onto the hydroxy-rich surface of cellulose fibers (Figure 7D).[76] Careful sequential adsorption and hydrolysis then enables deposition of a thin metal oxide layer and maintains nanoscale structural features. If the biotemplate does not readily adsorb metals, it can be modified through chemical functionalization, enzyme treatment, or mild hydrolysis.[77] Another approach is to decorate the biomass surface with noble-metal nanoparticles for surface-specific electroless deposition of metals.[78]

### *4.2. Biomaterials as a Dual-Function Template*

Organic biomass can be used both as a template and a carbon source for the production of metal carbides. This is typically achieved by first carbonizing the biomaterial (e.g. wood) and then infiltrating the resulting charcoal template with a liquid or gaseous metal reagent to form a metal carbide replica such as SiC, TiC, or ZrC.[79] Alternatively, the carbide can be produced in one step by soaking the biomaterial in an aqueous metal salt solution before pyrolysis.[80] In this case, the metal precursor first decomposes to give an oxide coating over the template before carbothermal reduction to give a carbide replica with the biological features still intact. By heating to a lower temperature (thus avoiding carbothermal

reduction), biomaterials can also be used to template carbon/metal oxide composites.[81] Another example that exploits the carbon-rich biomaterial as both a template and reducing agent is the formation of metal sulfides from cellulose fibers.[82]

## 5. Pyrolysis to Carbon Nanomaterials

Porous carbon materials have a wide range of current and potential applications, such as separation, water filtration, and supercapacitors. Many of these applications require specific properties, such as high porosity or heteroatom doping. As such, biopolymers are a particularly useful precursor, owing to their wide range of chemical functionality and tunable hydrogels. Furthermore, much of the biomass that is used to produce useful carbon materials is sourced from waste streams; thus the use of biomaterials is both sustainable and "value-adding". However, different biopolymers carbonize at different rates, which can lead to contraction and cracking in systems containing more than one component. As a result, a wide range of carbonization techniques have been developed.

### 5.1. Carbon Materials from Native Biomass

Such a large range of biomaterials have been carbonized that it is only possible to hint at the diversity of structures and functions. Most processes focus on agricultural waste products, since the potential applications often require cheap materials.[83] The simplest approach is pyrolysis of the native biomaterial under closed conditions or an inert atmosphere.[84] Alternatively, a two-step heating process can be used to initially strengthen the biopolymer network by crosslinking, for example, the synthesis of microporous N-doped carbon materials from chicken feather fibers (comprised of keratin, a fibrous structural protein also found in wool, hair, and some animal shells).[85] Another two-step strategy is to activate the carbon material after pyrolysis, either chemically (e.g. with KOH) or by heating in air to increase the porosity.[86] Metals can also be used to crosslink and stabilize the polymer precursor,[87] to increase porosity, or as catalysts (e.g. Fe or Ni) for graphitization of the carbon material at relatively low temperature.[88] The metal precursor can be introduced by infiltration, but many native biomaterials also contain metals (e.g. potassium in seaweeds) that have been exploited for in situ chemical activation.[89] As with many of the previous sections of this Minireview, the natural variability of biopolymers (e.g. between seaweed species) can be used to tune the exact properties of the carbon product. However, for some applications, such as supercapacitors, this lack of uniformity in biomass could cause problems with consistency of performance compared to carbon materials sourced from synthetic polymers.[90] In this case, the use of more homogeneous biopolymer hydrogels or alternative processing techniques, such as hydrothermal carbonization, may be a solution.[91]

### 5.2. Tailoring Biopolymer Gels for Tunable Carbon Materials

Applications such as catalysis or separation require carbon materials with a controlled pore-size distribution and accessible surface area. Traditionally, this is achieved by templating with, for example, mesoporous silica, which then requires dissolution with hazardous etchants like HF or caustic soda. Furthermore, the harsh conditions necessitate stable carbon materials with a high level of graphitization, which tend to have a relatively inert and hydrophobic surface. This issue has recently been addressed by using the inherent functionality and porosity of biopolymer hydrogels to synthesize carbon materials with controlled pore-size distribution and diverse surface chemistry. Aqueous starch gels were carefully dried, doped with a Brønsted acid catalyst to promote crosslinking, and then pyrolyzed under vacuum to produce mesoporous carbon monoliths (Starbons).[92] Since the porosity of the carbon material depends on the gel structure, materials with different pore size distributions could be prepared by using alternative polysaccharides, for example, alginic acid or pectin.[93] Furthermore, the chemical nature and hydrophilicity of the surface could be varied simply with calcination temperature, since increasing temperature eliminates more of the original polysaccharide oxygen content and introduces aromaticity.[94] Another attractive feature of these carbon materials is that they can be readily functionalized with, for example, $-SO_3H$ groups or metal nanoparticles to produce high-surface-area catalysts.[95]

## 6. Hydrothermal Carbonization

Hydrothermal carbonization (HTC) has undergone a renaissance in recent years.[96] This flexible process involves heating organic materials in water inside a sealed autoclave (generally $<300\,^{\circ}C$). The pressure generated during the process enables key chemical transformations to occur at relatively low temperatures. Depending on the carbon source, conditions, and presence of catalysts, HTC can be tailored to create a wide range of porous or nanostructured carbon materials with varied properties and functionality. Both biopolymers and native organic biomass have been targeted with the aim of producing value-added materials such as catalyst supports, filtration media, or supercapacitors from cheap and abundant sources. In this case, the real advantage of HTC processing of polysaccharides is the possibility to "fix" the heteroatom functionality of the biopolymers into the carbon material of the final product, thereby producing, for example, pyridine moieties. This sort of heteroatom doping into carbon material is increasingly of interest for energy storage and conversion applications. Alternatively, HTC could be considered a fast form of coalification, thus offering a route for carbon fixation from renewable biomass.

### 6.1. HTC of Simple Polysaccharides

HTC of mono- and disaccharides proceeds through multiple intermediates, such as furfural or organic acids,

which then undergo condensation and repolymerization.[97] In the absence of morphology-directing agents, HTC produces monodisperse spheres that consist of a hydrophobic polyaromatic core with a hydrophilic shell. Extending HTC to soluble biopolymers such as starch or alginic acid also results in solid carbon spheres through initial hydrolysis of the polymer to smaller fragments.[98] The average size of the carbon particles can be tailored to some degree (400 nm to 4 μm) by changing temperature and concentration. Furthermore, the addition of iron as soluble $Fe(NH_4)_2(SO_4)_2$ or $Fe_2O_3$ nanoparticles can produce hollow spheres or fibers, respectively.[99] HTC of nitrogen-rich biopolymers, for example, chitosan, produces carbon spheres with a high nitrogen content (9%).[100] Water-insoluble biopolymers such as cellulose require higher temperatures and longer heating times to achieve carbonization.[101] As such, low-temperature HTC of cellulose produces only a small amount of colloidal carbon from surface dissolution. The primary mechanism of cellulose carbonization is believed to be direct intramolecular condensation within the cellulose matrix.[102] A combination of HTC of polysaccharides with metal precursors can be used to produce nanocomposite metal/carbon materials, for example, tellurium nanowires[103] or core–shell silver–carbon nanowires,[104] which maintain almost the same conductivity as the bulk metal. Here the biopolymer is carbon source, structure-directing agent, and reducing agent for the metal. Furthermore, since HTC produces materials with an oxygen-rich hydrophilic surface, these can be used for further templating, for example, of hollow spheres of metal oxides.[105]

### 6.2. HTC of Native Biomaterials

The complex mixture of biopolymers in many native biomaterials introduces some challenges for HTC, since the different components degrade and carbonize at different rates. However, the benefits of carbonizing raw biomass are clear: it is possible to generate useful carbon materials directly from low- or negative-value materials. A wide range of biomass has been investigated. For example, carbonization of oak leaves produced a sponge-like mesoporous structure, whereas pine needles made aggregated carbon nanoparticles (20–200 nm).[106] In general, woody lignocellulose materials maintain their intact macrostructure, and it is believed that the lignin remains relatively unchanged while the cellulose is carbonized. As with HTC of single biopolymers, time, temperature, pressure, and the presence of catalysts are all key to the final structure. HTC can also be used to "fix" nitrogen from biomass within a polyaromatic carbon network. Thus HTC of protein-rich microalgae or chitin-based prawn shells produces carbon material with incorporated pyridine and pyrrole species.[107] The added advantage of sources such as prawn shells (along with all other crustaceans) is that they are a composite of chitin fibers with calcium carbonate crystallites (Figure 8A).[108] Thus the inorganic phase also acts as an in situ template, which can be removed after carbonizing by dissolving in dilute acid to generate highly porous carbon materials (Figure 8B).

## 7. Harnessing Natural Variability—Making the Most of a Flexible Resource

This Minireview has explored the diverse applications of biological macromolecules in nanostructure synthesis. Many of the examples rely on common chemical and structural features such as metal-binding functionality or formation of extended networks. Depending on the conditions, these features can be harnessed to direct crystal growth, introduce porosity, or produce porous carbon materials. Most current examples use biopolymers that are extracted from a mixture of sources. However, the structure and composition of animal and plant biopolymers can change dramatically between species, habitats, and even within different parts of the same organism. This can strongly affect properties such as metal binding, gel strength, and decomposition temperature. While natural variation in biomaterials requires care, it can be extremely useful in tuning properties. This variability is used widely in other fields such as food science, biotechnology, and pharmaceuticals, but there are comparatively few examples in nanochemistry. Certainly, there are commercial sources of specialized biopolymers, but sometimes it is necessary to look further than the chemistry catalogues! Another potential issue with biological sources is the presence of impurities, for example, plants often sequester traces of various metals. This might seem aberrant to chemists who are accustomed to high-purity materials, but we have seen that even the presence of impurities such as metallic species can be used to an advantage, for example in activating carbon materials. A final challenge is processing. Many biopolymers form very

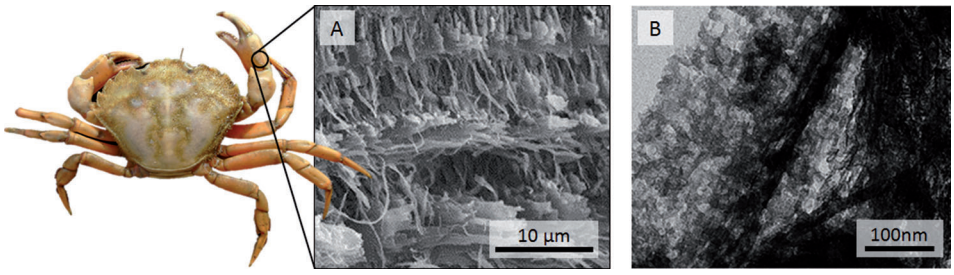



***Figure 8.*** A) Typical structure of fibrous chitin with matrix proteins and $CaCO_3$ crystallites in crustacean shells. B) Porous carbon material produced by HTC and calcination of prawn shells followed by acid dissolution of $CaCO_3$. Adapted with permission from references [4] and [107a], respectively.

viscous solutions or gels at quite low concentrations in water and so a judicious choice of molecular weight or derivative may be necessary. On the other end of the scale, some biopolymers display extremely low or zero solubility, but again, there are potential solutions such as dissolution of cellulose in ionic liquids.[109]

Finally, are biopolymers green? They are sourced from renewable feedstocks and many are abundant or even waste products. Furthermore, they are generally biodegradable and nontoxic. There are many examples of biopolymer-based material synthesis in the literature that claim the method is "green". However, it is perhaps too simplistic to state that a natural resource is inherently more sustainable than polymers synthesized from fossil feedstocks. Some biopolymers require quite lengthy extraction processes that could hardly be called green. Direct use of biomass circumvents this problem, but there are many other factors that may affect sustainability such as changing land use, or collection and purification of a dispersed waste source. It is important to consider a full life cycle analysis and indeed there may be wider opportunities for green chemistry in developing alternative biopolymer extraction techniques. Certainly, biopolymers offer an exciting, flexible, and largely unexplored resource for materials chemistry.

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