

Green Synthesis of Inorganic–Organic Hybrid Materials: State of the Art and Future Perspectives

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Abstract: The term “inorganic–organic hybrid materials” designates inorganic building blocks in the colloidal domain (1–1000 nm) embedded in an organic, typically polymeric, matrix. Owing to their outstanding properties, hybrid materials have the potential to improve human life significantly. In the last two decades, the importance of reorienting chemical syntheses in the direction of more sustainable, less harmful and energy-consuming procedures referred to as green chemistry has been

much emphasized and worked on. This review deals with the application of green chemistry to the synthesis of inorganic–organic hybrid materials. The origin and preparation both of the inorganic components and of the organic polymer matrix are critically analyzed for various examples. The development of more sustainable syntheses for hybrid materials still poses an open challenge. Potential options to tackle this task are discussed.


1. Introduction

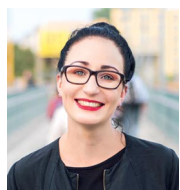
The term “hybrid” – in its current use – originates from the Latin “hybrida,” meaning mixed-breed. A hybrid material is indeed composed of at least two different materials, resulting in both components contributing to the properties of the final hybrid material. Most interestingly, “hybrida” itself is actually of ancient Greek origin, with “ὑβρις” meaning “arrogance” in its negative literal sense, but also referring to the positively connoted “strength”/“power”.^[1] As a matter of fact, one might describe an ideal hybrid material as a crossover of the properties of several components into a *powerful* material that maximally benefits from the assets of its components. Indeed, the properties provided by hybrid materials are more than the mere sums of features of their components. This is commonly attributed to the interface between the components,^[2] which one might think of as “third component” owing to its impact on the hybrid material. In particular for hybrid materials with at least one component in the colloidal domain (1–1000 nm), the interfacial area is much larger than for macrocomposite materials, making its contributions even more important.

Inorganic–organic hybrid materials (i.e., materials with an inorganic component “dispersed” in a major organic, typically polymeric, component) are the scope of this review. Historically, such materials were first conceived to enhance the properties of polymers.^[3] For instance, inorganic fillers such as clay mineral particles enhance the mechanical strength of the polymer matrix and can also generate, for example, barrier and flame-retarding properties.^[4] In addition to structural reinforcement, a plethora of physicochemical features can be contributed by the inorganic compounds, including magnetism, electric conductivity, and catalytic and/or redox activity. In the last decades much effort has been put into designing highly sophisticated hybrid materials that provide such outstanding features, thus surpassing mere mechanical reinforcement. Hybrid materials offer outstanding potential for benign technologies, such as solar energy, fuel cells, rechargeable batteries, and electronic devices of increased efficiency.^[5] Thus, these materials will ultimately improve human quality of life and reduce our dependency on fossil fuels, as well as our harm to the environment. But does the end justify the means? How benign are the syntheses of these “wonder materials”? And more importantly, how much room is there for improving the currently used procedures?

This article aims to address these questions for the area of inorganic–organic hybrid materials. To date, there is no literature review of green syntheses of hybrid materials. This review aims to bridge this gap. To ensure readability both for readers with a background in green chemistry and for those with solid

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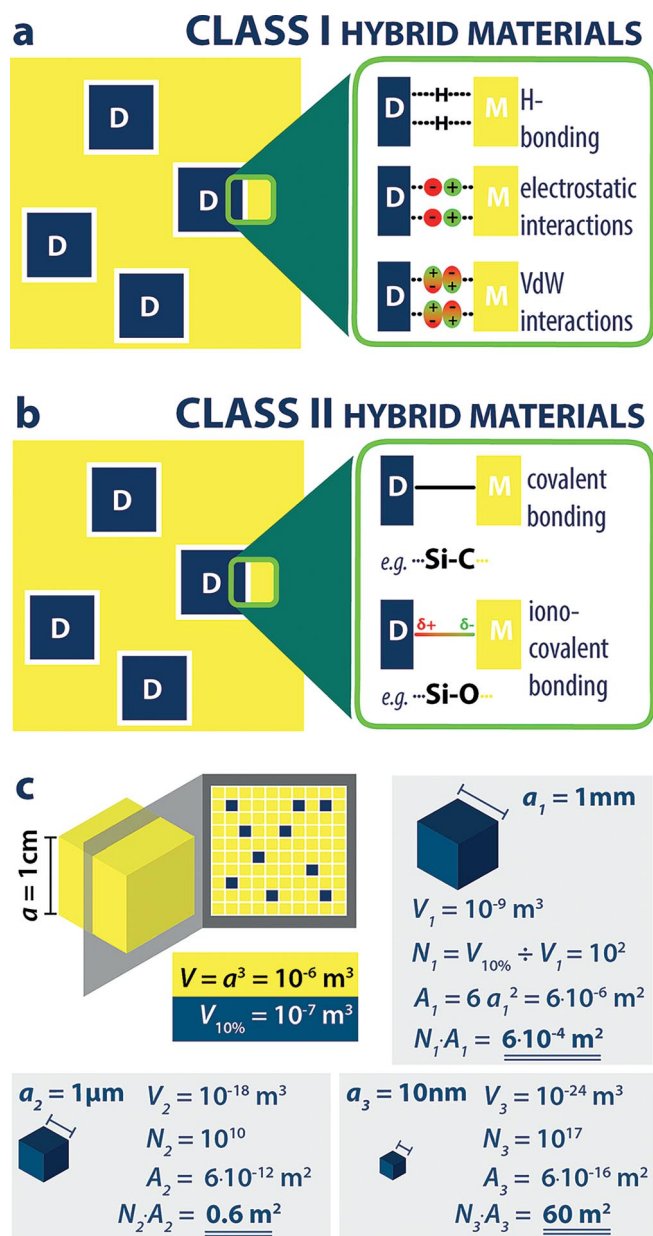
knowledge of hybrid materials, both fields are first briefly introduced, and basic definitions are summarized (Section 2). The topic of hybrid materials includes several subclasses, which cannot all be covered in this article. Therefore, this review will have to concentrate on one aspect: namely, inorganic–organic hybrid materials with the inorganic components in the colloidal size range, “dispersed” in an organic polymer matrix as the major component. Because both the origins and the syntheses of both the inorganic and the organic components can be “green” or not, each is first analyzed separately. The following subsections are designated to cover this: green routes towards inorganic colloids (Section 3.2), inorganic colloids from renewable resources (Section 3.3), green polymerization techniques (Section 3.4), and polymers from renewable resources (Section 3.5). In Section 3.6 examples of inorganic–organic hybrid materials in which at least one green step or component is implemented are critically analyzed. It will become clear that despite significant development in the sustainable syntheses of the inorganic and organic macromolecular components, there is still a significant way to go for hybrid material synthesis.

2. Definition of “Inorganic–Organic Hybrid Material” and “Green Chemistry”

The International Union of Pure and Applied Chemistry (IUPAC) defines a hybrid material as a “material composed of an intimate mixture of inorganic components, organic components, or both types of components”, noting that “the components typically interpenetrate on scales of less than 1 μm ”.[6] This definition includes, for example, polymer–polymer composites (*aka* blends), metal–metal composites, metal–ceramic composites, metal–polymer, and ceramic–polymer composites. The plethora of *powerful* hybrid materials cannot be covered in one review article. This paper will thus focus on one subclass of hybrid materials: namely, inorganic–organic hybrid materials in which the amount of organic polymeric component is a majority over that of the inorganic component. Note that the term “composite” historically tends to be associated with macroscopic hybrid materials with the dispersed phase typically greater than 1 mm. Others associate “composite” with hybrid materials in which the components interact through noncovalent bonding, and “hybrids” with cases in which the components are connected by covalent bonding.[7] In recent years, this distinction has faded more and more, and both terms are often used interchangeably. This review addresses exclusively inorganic–organic hybrid materials with the minor component in the colloidal range, and the term “composite” is used occasionally.

Depending on the strength of interaction between the dispersed inorganic phase and the organic matrix, hybrid materials are commonly subdivided into two categories.[2] In class I hybrid materials there are weak interactions – namely, van der Waals (vdW), hydrogen bonding, and electrostatic interactions – between the components (Scheme 1, a).[2] Class II hybrid materials display strong bonding (i.e., covalent or ionic-covalent interactions, Scheme 1, b);[2] ionic-covalent interactions are covalent bonds with a considerable ionic character often found, e.g., in binary or mixed metal oxides).[8] In class II hybrids, the strong

interactions might of course be accompanied by weak interactions characteristic of class I hybrids.[2]



Scheme 1. Categories of hybrid materials and importance of the D–M interface. D = dispersed phase, M = matrix. (a) Class I hybrid materials exhibit weak interactions between D and M. From top to bottom: H-bonding, electrostatic interactions, or van der Waals (vdW) interactions. (b) Class II hybrid materials are characterized by strong interactions (i.e., covalent and ionic-covalent bonding). (c) Interfacial area in a cube of hybrid material of 1 cm edge length a , containing 10% by volume of a size-monodisperse cubic dispersed phase (supposition: D neither agglomerates nor touches the surface of the cube) of different edge lengths $a_1 = 1 \text{ mm}$, $a_2 = 1 \mu\text{m}$, $a_3 = 10 \text{ nm}$.

Spatially speaking, the interactions between dispersed phase (D) and matrix (M) are located at the interface between the M and D. When D lies in the colloidal domain, the interface is much more important than in macroscopic hybrid materials. If we consider a cube of a hybrid material with 1 cm edge length, reinforced with cubic dispersed particles of edge length 1 mm and accounting for 10% of the volume, the M/D interface

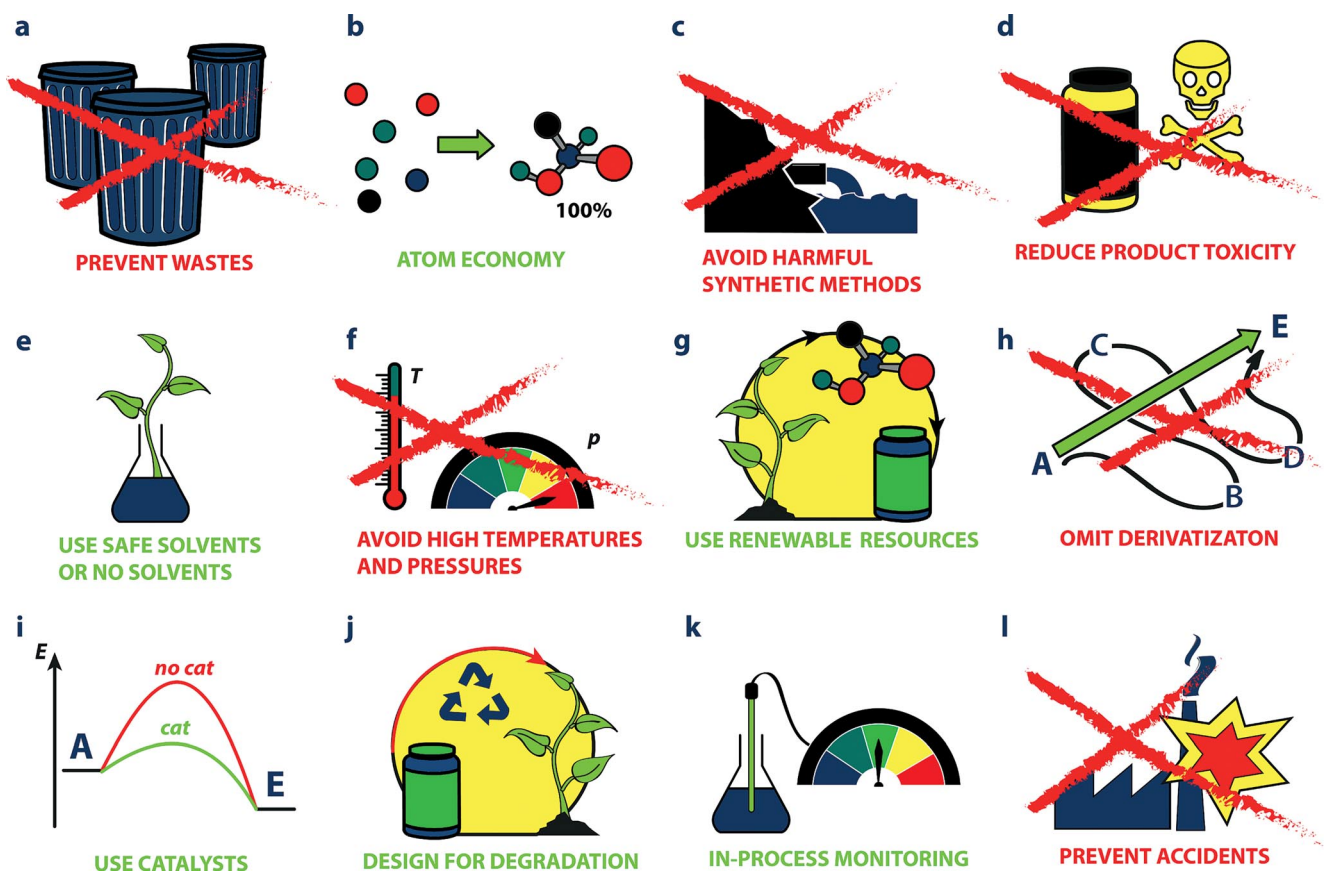
would be of $6 \times 10^{-4} \text{ m}^2$ or 60 cm^2 (Scheme 1, c). On decreasing the edge length of the dispersed cubes to $1 \mu\text{m}$, the upper limit of the colloidal range, we already end up with 0.6 m^2 or 6000 cm^2 of M/D interface. On decreasing D even further to an edge length of 10 nm – and thus into the nanodomain ($1\text{--}100 \text{ nm}$) – there would be 60 m^2 , or 600000 cm^2 , of interface inside our 1 cm^3 piece of hybrid material (Scheme 1, c). Such important interfacial areas are highly beneficial in processes that take place precisely at the interface. One example from the field of inorganic–inorganic hybrid materials is carbon nanotube (CNT)–transition metal oxide hybrids for photocatalysis applications.^[9] For instance, in photocatalytic water splitting in CNT/ Ta_2O_5 hybrids, much higher activities for H_2 evolution than in pure tantalum oxides have been found, and were attributed to the interface.^[10]

Although this review focuses exclusively on inorganic–organic hybrid materials with the organic component being polymeric and present to the major extent, there are numerous other types of hybrid materials in which inorganic and organic compounds are united. Such hybrids include, for instance, interpenetrating networks of inorganic and organic polymers (referred to as “type III” hybrids by Novak),^[2,3,11] low-molecular-weight organic components (e.g., organic dye molecules) embedded in an inorganic matrix,^[2,12] inorganic–organic core-shell colloidal particles,^[3a] or cluster-cross-linked polymers.^[13] The in-

terested reader is directed to the corresponding references that excellently cover these topics.

In recent decades people have become increasingly aware of the limitedness of fossil fuels and scarce metals, and of the dangers to human health and the environment when recovering these finite resources. Clearly, the harm caused to date cannot be undone. However, it is commonly agreed on that our dependency on fossil fuels has to decrease, and that we have to change our procedures for recovering resources, producing energy, ensuring transportation, and building machines and buildings. Inevitably this also means changing the fabrication of the materials from which these machines, vehicles, and buildings are made, towards fully sustainable routes.

In the field of chemistry, this goal has culminated in “green chemistry”. The term was coined by Anastas,^[14] and is described not by a simple definition, but by a set of 12 principles first summarized by Anastas and Warner.^[15] These principles are also recommended for use by the IUPAC subcommittee on green chemistry.^[14] Below we go through the 12 principles, which are also summarized in Scheme 2. Poliakoff and co-workers have recommended the use of condensed forms to improve memorability,^[16] and such short forms are also used by, for example, the American Chemical Society.^[17] According to this recommendation, condensed forms are given in addition to the initial principles in brackets below.



Scheme 2. The 12 principles of green chemistry. (a) Prevent waste (#1), (b) atom economy (#2), (c) avoid harmful synthetic methods (#3), (d) reduce product toxicity (#4), (e) use safe or no solvents (#5), (f) avoid high temperatures and pressures (#6), (g) use renewable resources (#7), (h) omit derivatization (#8), (i) use catalysts (#9), (j) design for degradation (#10), (k) in-process monitoring (#11), (l) prevent accidents (#12).

(#1) It is better to prevent waste than to treat or clean up waste after it is formed (prevent wastes). The commonly used metric to evaluate amounts of generated waste is the so-called *E*-factor (environmental factor) introduced by Sheldon.^[18] The *E*-factor is the quotient of mass of generated waste (unit kg) per mass of product. Highest waste generation is found in the synthesis of pharmaceuticals, with *E*-factors of 25–100.^[18b]

(#2) Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product (atom economy). The metric of “atom economy” (given in %) was developed by Trost and is defined as the quotient of the formula weight of the desired product with the sum of formula weights of all reactants.^[19] Atom economy accounts for possible byproducts and waste. Note that for a reaction $A + B \rightarrow C + D$, with C the desired product and D a byproduct, the atom economy can be quite low (depending on the molecular weights of A, B, C, and D) even if the reaction is quantitative.

(#3) Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment (avoid harmful synthetic methods). This principle focuses on benign methodologies. If byproducts cannot be avoided, they should at least be innocuous. One example with respect to hybrid materials is the generation of SiO₂ by polycondensation of silicic acid, yielding H₂O as harmless byproduct.

(#4) Chemical methods should be designed to preserve efficacy of function while reducing toxicity (reduce product toxicity). Substituting harmful substances by innocuous ones while maintaining functionality is challenging, but often feasible. For instance, the synthesis of hybrid materials often requires surfactants for compatibilizing the inorganic and the organic components. As is discussed further in Section 3.6, several surfactants that originate from renewable resources and are biocompatible and biodegradable are already an option.^[20]

(#5) The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary whenever possible and innocuous when used (use safe or no solvents). Solvents often account for up to 85 % of the total mass in a reaction mixture.^[21] Approaches for substituting harmful solvents (e.g., chlorinated solvents) include the use of ionic liquids,^[22] supercritical CO₂,^[22,23] and H₂O.^[24] The reader interested in the evaluation of common solvents is directed to a solvent selection guide in which these solvents are assessed with respect to waste generation, human health, and impact on the environment and safety issues.^[25]

(#6) Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure (avoid high temperatures and pressures). Although excess heat generated by one reaction step can be used in another step,^[26] this is hardly workable on a research lab scale. Therefore, high temperatures and pressures should be avoided. This is, however, sometimes poorly compatible with the use of alternative solvents: for example, using high-temperature water demands important energy input.^[27]

(#7) A raw material or feedstock should be renewable rather than depleting wherever technically and economically prac-

ticable (use renewable resources). To measure amounts of used renewable feedstock, Henderson et al. have recently proposed the metric of “renewables intensity”, defined as the mass of all used renewably derived materials (in kg) per kg of product.^[28] As is discussed in Section 3, this principle can already be met to an impressive extent in the synthesis of organic polymers.

(#8) Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible (omit derivatization). Any derivatives on the pathway to the target molecule require additional reagents and generate additional waste and should therefore be avoided when possible. The extent of derivatization is indirectly accessible through the metric “atom economy” (see principle #2).

(#9) Catalytic reagents (as selective as possible) are superior to stoichiometric reagents (use catalysts). Catalysts are by definition used in catalytic amounts and are thus important with respect to atom economy (see principle #2). In addition, transition-metal catalysts in particular often impart selectivity (chemo-, regio-, diastereo-, and enantioselectivity) and lower the required energetic input by lowering the activation energy of a transformation.^[19a] Because transition metals are scarce resources, the use of enzymes – which are renewable biocatalysts – has recently received much attention.^[29] With respect to the synthesis of hybrid materials, the use of enzymes is relevant for the preparation of the organic polymer component.^[30]

(#10) Chemical products should be designed so that, at the end of their function, they do not persist in the environment but break down into innocuous degradation products (design for degradation). Degradability is extremely desirable for products that can persist in the environment for hundreds of years, such as petroleum-based plastics.^[31] As further discussed in Section 3, numerous biodegradable polymers have already been reported.^[31b]

(#11) Analytical methods need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances (in-process monitoring).

(#12) Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires (prevent accidents).

Clearly, there is no way of prioritizing these principles. On the contrary, the importance of the different principles depends on the precise task. Moreover, all principles are hardly fulfilled for one chemical reaction. Consider, for instance, the recently much envisioned approach of replacing the predominance of fossil oil and gas by methanol, the so-called “methanol economy”.^[32] Methanol can be generated from renewable resources and converted into many other chemicals in catalyzed, quantitative reactions. However, methanol itself is toxic. Other examples are supercritical CO₂ or H₂O as solvents.^[27,33] Both are commonly considered “green” and environmentally friendly solvents. Yet, to reach the supercritical regime, one has to operate at considerable pressures (and temperatures for H₂O), which is energy-intensive in relation to working under ambient conditions.

3. Green Synthesis of Inorganic–Organic Hybrid Materials

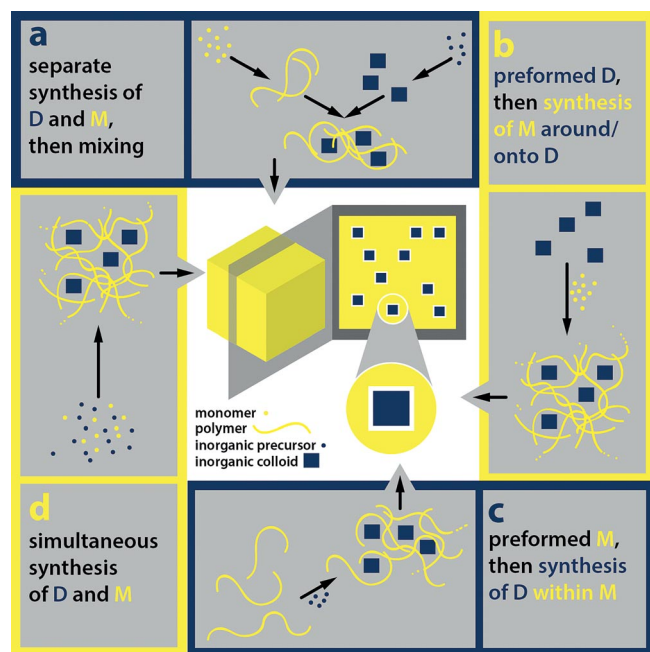
In the following sections, firstly, the synthetic steps involved in the preparation of inorganic organic hybrid materials are discussed in a general fashion (Section 3.1). Secondly, green options for each of the involved steps are reviewed (Sections 3.2–3.5). Thirdly, in Section 3.6, examples of hybrid materials based on one or more green steps are discussed in detail. Finally, open challenges and perspectives are analyzed in Section 3.7.

3.1. Overview of Synthetic Steps in the Preparation of Hybrid Materials

For the simplest case of a binary inorganic–organic hybrid material, there are two components: the matrix (M, here organic polymeric) and the dispersed phase (D, here inorganic). By definition, D lies in the colloidal domain (1–1000 nm) and might variously be a particle (i.e., with all three spatial directions in the colloidal range), a fiber (i.e., with two spatial directions in the colloidal range), or layered (i.e. with only one spatial direction in the colloidal range) (cf. also Section 3.2 and Scheme 4).^[34] Moreover, D can be either crystalline or amorphous. The synthetic approaches for combining D and M can be subdivided into four categories: (i) separate synthesis of D and M, followed by a combination step (Scheme 3, a), (ii) preformed D, followed by synthesis of M around/on D (Scheme 3, b), (iii) preformed M and synthesis of D from/inside the polymer (Scheme 3, c), and (iv) simultaneous formation of D and M (Scheme 3, d). These four general synthetic approaches to hybrid materials can be used to produce both class I and class II hybrids (cf. Scheme 1), and can also additionally require the use of additives. For instance, the approach of using preformed inorganic and polymeric components can lead to class II hybrids if so-called reactive mixing is used. This involves the functionalization of the

inorganic D and of the polymeric M with complementary moieties that, upon reaction with one another, lead to the formation of covalent bonds. Such moieties can, for instance, be alkynes and azides, which react to produce triazole moieties through copper-catalyzed 1,3-dipolar Huisgen cycloaddition, thus enabling the formation of class II hybrids.^[35] The formation of M around a preformed D is very common for reinforcing polymeric matrices with phyllosilicates, such as the clay minerals montmorillonite or kaolinite. The layered structure of phyllosilicates requires exfoliation, which can be directly generated through infiltration with monomers that push the galleries apart when polymerizing, typically yielding class I hybrids.^[3a] Polymerization from (“grafting from”) the inorganic colloids is possible by covalently attaching moieties that mediate controlled radical polymerizations, such as reversible addition–fragmentation chain-transfer polymerization (RAFT) or atom-transfer radical polymerization (ATRP) to the inorganic D.^[3a] The preparation of the inorganic component inside a preformed polymer is a less common approach, and typically requires moderate conditions in order to ensure that the organic polymer remains intact. Such mild conditions (at least with respect to the synthesis temperature) are used in hydrolytic sol-gel approaches involving metal alkoxides. Nunes et al. used a sol-gel approach for generating hybrid materials of sulfonated poly(ether ether ketone) (SPEEK) with several metal oxides (SiO₂, TiO₂, ZrO₂).^[36] In their approach, SPEEK was infiltrated with the corresponding metal alkoxide and gently transformed (e.g., 16 h at room temperature for TiO₂ and ZrO₂) into colloidal metal oxide particles embedded in the polymeric matrix.^[36] The simultaneous formation of D and M is most often achieved by using hybrid precursors that can be copolymerized with additionally supplied organic monomers on one side, and form the inorganic species on the other side. A widely used class of such hybrid precursors are derived from tetraethoxy silane (TEOS) by substitution of one ethoxide moiety with a function that can be (co-)polymerized with an organic monomer. Such functions include, for instance, acrylate or methacrylate groups.^[3a]

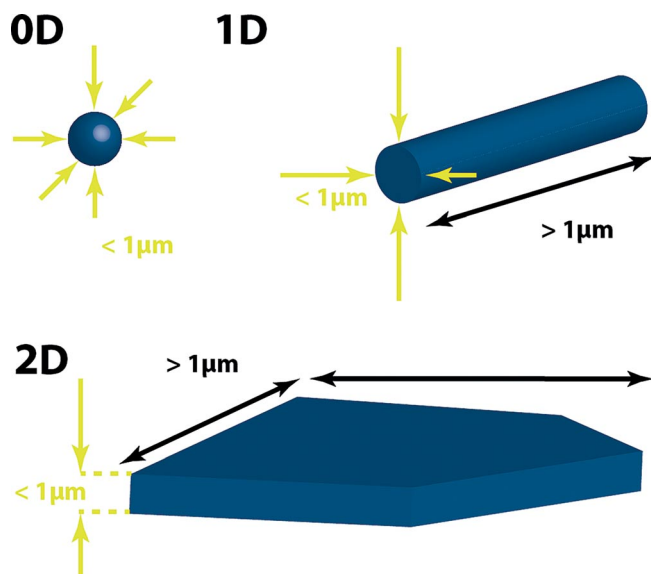
As a consequence of the four general synthetic approaches to inorganic–organic hybrid materials, there are several involved species and synthesis steps that can be “green” or not. For instance, consider the synthesis of a hybrid material from preformed D and M (cf. Scheme 3, a). The precursor of D can be of renewable origin or not, the synthesis of D from the precursor can be green or not, the monomer of M can be from renewable resources or not, the polymerization can be green or not, and the mixing step of D and M can be green or not. Combinatorically speaking, there would be $5^2 = 32$ possibilities of how green this route can be, if the simplifying black-and-white assumption that there is only “green” or “not green” is made. In order to cover the different steps involved in the best cases, below we go through the following topics: green synthesis of inorganic colloids (Section 3.2), inorganic colloids from renewable resources (Section 3.3), green polymerization techniques for organic polymers (Section 3.4), and monomers from renewable resources (Section 3.5). Examples of inorganic–organic hybrid materials that are “green” in at least one step are reviewed in Section 3.6.



Scheme 3. The four general synthetic approaches to inorganic–organic hybrid materials (a–d) D = dispersed phase (inorganic), M = matrix (organic, polymeric).

3.2. Green Synthesis of Inorganic Colloids

The inorganic component in an inorganic–organic hybrid material can be classified according to the number of dimensions (or, better, spatial directions) lying outside the colloidal domain: as 0D (particles), 1D (fibers), and 2D (layers) (see Scheme 4).^[34]



Scheme 4. Classification of colloidal objects according to dimensionality. (a) 0D: zero dimensions are outside of the colloidal domain (i.e., all three spatial directions are inside the colloidal domain). (b) 1D: one spatial direction is inside (black arrow) and two are outside (yellow arrows) the colloidal domain. (c) 2D: two spatial directions are outside (black arrows) and one is inside (yellow arrows) the colloidal domain.

0D inorganic colloids are particles smaller than 1 μm in diameter. Shapewise they can be spherical or non-spherical (i.e., shape-anisotropic). Examples include metal or metal oxide particles. Metal (nano)particles are typically synthesized either chemically by so-called bottom-up approaches or physically by top-down techniques.^[37] A much applied top-down technique, for example, is the grinding of bulk solids into nanoparticles (NPs) by high-energy ball milling.^[38] Bottom-up approaches are mainly carried out by wet chemistry. For metal NPs, this involves reducing a salt that contains the corresponding metal as cation. For instance, to synthesize gold nanoparticles, the most widely applied procedure is the reduction of chloroauric acid (HAuCl_4) with reducing agents such as NaBH_4 or citrates.^[39] Green syntheses of metal NPs have attracted much interest recently, especially in the context of toxicity. The harsh chemicals used in wet-chemistry syntheses are believed to adsorb to the particle surfaces and to contribute to their toxicity.^[40]

3.2.1. Organism-Mediated Synthesis of Metal and Metal Oxide Nanoparticles

One green approach to producing metal nanoparticles involves biosynthetic techniques, either *in vivo*, involving organisms such as bacteria, yeasts, fungi, algae, or plants, or by using non-living biomass such as plant extracts (cf. Table 1).^[40] The approach comes as no surprise: numerous organisms are known to possess the ability to produce inorganic materials, and have been studied in the context of biomineralization.^[41] Examples include the synthesis of magnetite (Fe_3O_4) by magnetotactic bacteria^[42] or of silica (SiO_2) by diatoms,^[43] as well as CaSO_4 mineralization of cell surface layers by certain bacteria.^[44] Many

Table 1. Comparison of green syntheses of inorganic colloids.

Method	Accessible materials	Synthetic conditions	Ref. (selection)
Ambient wet chemistry (benign reducing agents and stabilizers)	NPs of: Ag, Ag/TiO ₂ , Fe ₃ O ₄ , Fe ₃ O ₄ /Au, Au–Ag bimetallic	reduction of metal ions with benign reducing agents of low (e.g., β -D-glucose, ascorbic acid) or high (e.g., polysaccharides) molecular weight; typically the reducing agent is added to an aqueous salt solution, which is kept stirring at the desired T for a few minutes to hours.	[61–69]
<i>In vivo</i> (plants)	NPs of: Cu, Ag, Au, Pd, Au–Ag–Cu alloy	seedlings of, for example, alfalfa are grown in metal-ion-containing growth media at ambient T and p ; growth periods of days/weeks; NP isolation by pyrolysis of the plant material or chemical leaching.	[45–47]
<i>In vivo</i> (yeasts, fungi)	NPs of: Au, Ag, CdS	preparation of a dispersion of the fungus/yeast in an aqueous solution containing the needed precursor ions; mixture is kept at conditions under which the fungus grows well (e.g., 28 °C, stirring, 72 h)	[54–56]
Plant-mediated (plant extracts)	Au, Ag, Au–Ag bimetallic, Fe ₃ O ₄ , Fe _{0.902} O	preparation of a solution containing the precursor ions and subjecting it either to the pure plant extract or to a solution/dispersion of the plant extract or milled plant material; mixture is stirred or rested at ambient T and p for a few hours	[40,48–52,56b]
Yeast/fungi-mediated (extracellular)	NPs of Au, Ag, CdS, TiO ₂ , SiO ₂ , Fe ₃ O ₄ , BaTiO ₃	preparation of a dispersion of the fungus/yeast in an aqueous solution containing the needed precursor ions; mixture is kept at ambient T and p for several hours	[56b,58–60]
Hydrothermal synthesis	zeolites, non-zeolitic aluminosilicates, metal oxides, phosphates, chalcogenides, hydroxides, perovskites, MOFs, coordination polymers, clay minerals	preparation of a precursor solution or dispersion containing ion sources and additives (e.g., for pH adjustment, as templating agents); this dispersion is heated to the HT regime ($T > 100$ °C, $p > 1$ bar), kept there for a few hours to several days, and subsequently allowed to cool back to ambient conditions (often by slow cooling).	[72–82]

plants have the ability to accumulate heavy metals and are thus interesting candidates for the synthesis of metal and metalloid NPs.^[40] NP compositions that can be obtained by organism-mediated synthesis include metals (Cu, Ag, Au, Pd) as well as metal oxides (ZnO, In₂O₃, Fe₃O₄).^[40] Gardea-Torresdey et al. reported the synthesis of crystalline Au nanoparticles in vivo in alfalfa (*Medicago sativa*) sprouts.^[45] Alfalfa seeds were immersed in an aqueous nutrient solution containing various ions (Ca²⁺, K⁺, Mn²⁺, NO₃²⁻, Cl⁻, H₂PO₄⁻, SO₄²⁻, etc.) and KAuCl₄ as gold precursor. The alfalfa sprouts were grown over two weeks in a growth chamber with use of 12 h photoperiods, and this led to crystalline NPs of 2–15 nm in diameter.^[45] Haverkamp et al. reported the production of Au-Ag-Cu alloy NPs in leaf mustard (*Brassica juncea*) plants by growing the plants in soils enriched with AuCl₃, AgNO₃, and CuCl₂ over nine weeks.^[46] This approach is an example of using plants for decontamination of heavy-metal-polluted ground, and at the same time synthesizing metal NPs.^[45] Sharma et al. showed that rattlebush (*Sesbania drummondii*) seedlings could be used for the growth of Au NPs: after only six days in a HAuCl₄-containing growth solution spherical NPs of 6–20 nm in size could be harvested.^[47] Common procedures for isolation of NPs grown in vivo include, for example, freeze-thawing or chemical leaching.^[40] Unfortunately, though, these procedures can destroy the NP structures.

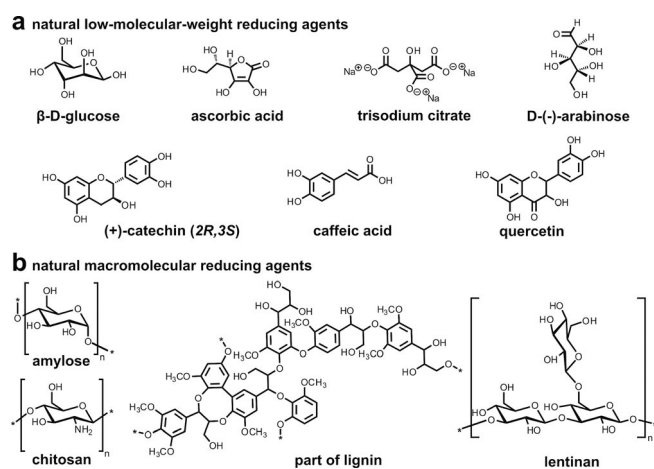
As well as in vivo synthesis, plant extracts have been used for the preparation of metal and metal oxide NPs.^[40] Such organism-assisted syntheses in which the NPs are not grown inside an organism are sometimes also referred to as “extracellular”. The plant extracts typically serve as reducing agents, thus substituting, for example, NaBH₄ in classical wet-chemistry NP synthesis. Shankar et al. used geranium (*Pelargonium graveolens*) leaf extract as reducing agent in the synthesis of Au NPs and observed that the reaction was complete after 60 min.^[48] In their procedure, the plant extract was added to an aqueous solution of HAuCl₄, thereby reducing Au^{III} to Au⁰.^[48] Herrera-Becerra et al. applied an alfalfa-mediated extracellular approach to synthesize Fe₃O₄ and wuestite (Fe_{0.902}O) NPs by treatment of an aqueous ammonium iron sulfate solution with an aqueous milled alfalfa dispersion for 48 h at room temperature.^[49] Ag and Au NPs have also been prepared by using extracts from other plants, such as Indian gooseberry (*Emblica officinalis*),^[50] neem (*Azadirachta indica*),^[51] or tamarind (*Tamarindus indica*).^[52] In general, such plant extracts are complicated mixtures of proteins, enzymes, small-molecule compounds (carboxylic acids, amino acids), vitamins, polysaccharides, etc., and the precise reduction mechanisms are therefore typically not known.^[40] However, it is likely that certain functions prevalent in bioorganic molecules, such as amino or carbonyl groups, coordinate to the metal cations prior to reduction.^[53]

As well as plants, yeasts and fungi have also been shown to be able to synthesize NPs of CdS,^[54] Au,^[55] or Ag^[56] in vivo. The actual NP syntheses are impressively benign: for example, for Ag synthesis, a dispersion of the used fungus in an AgNO₃ solution is simply stirred at 28 °C for 72 h.^[56a] Fungi and yeasts can also be used for the extracellular synthesis of NPs of metals (Au, Ag),^[56b] binary compounds such as CdS,^[57] TiO₂ and SiO₂,^[58] ZrO₂,^[59] or Fe₃O₄,^[56b] and even of the ternary BaTiO₃.^[60] The

corresponding syntheses were all carried out at ambient *T* and *p* in aqueous solutions for only a few hours.

Both in and ex vivo plant-mediated biosynthetic approaches to NPs can be qualified as green, not only because of the renewable origins of the reducing agents, but also because of the very moderate conditions (i.e., ambient *T* and *p*) and aqueous solutions. Have these techniques, however, been implemented in green inorganic–organic hybrid materials synthesis? To the author's best knowledge, there is to date only one example: the very elegant preparation of Pd NPs inside a carbonaceous matrix, and the application of this hybrid material for catalysis (see Section 3.6).^[53] Potential reasons for plant-grown/mediated NPs not finding much implementation in hybrid materials are further discussed in the last section of this review (Section 3.6).

Green synthesis of metal NPs can also be achieved by using benign reducing agents that are not an organism or an extract of an organism (Table 1). Such approaches replace common reducing agents, such as NaBH₄, by harmless compounds. Wallen and co-workers reported the synthesis of Ag NPs by use of β-D-glucose as reducing agent (Scheme 5, a), and soluble starch as stabilizer.^[61] Their approach consists of preparing an aqueous solution of AgNO₃, starch, and β-D-glucose, and stirring this solution for 20 h at 40 °C. The procedure can be modified by additionally using sodium citrate (Scheme 5, a),^[62] or by using other sugars such as D-(–)-arabinose (Scheme 5, a).^[63] By heating the sugar-containing Ag^I solutions to boiling, optionally by microwave heating, the reaction times can be shortened to a few minutes.^[62,63] Bashir and co-workers have recently reported the synthesis of Ag/TiO₂ composite NPs with the aid of food products as reducing agents. They used TiO₂ NP dispersions in aqueous AgNO₃ solutions, which were reduced by stirring at room temp. for 2 h with the reducing agents orange juice, coffee, jasmine tea, or prune juice.^[64] The active reducing species in these products are ascorbic acid (i.e., vitamin C, orange juice), catechins (coffee and prune juice), phenolic acids (jasmine tea, prune juice), flavonoids (prune juice), and proanthocyanidines



Scheme 5. Selection of natural reducing agents. (a) Low-molecular-weight reducing agents: exemplarily depicted are β-D-glucose, ascorbic acid (vitamin C), trisodium citrate, D-(–)-arabinose, (+)-catechin (2*R*,3*S*), caffeic acid (a phenolic acid), and quercetin (a flavonoid). (b) Macromolecular natural reducing agents: exemplarily depicted are amylose (major component of starch), chitosan, a small part of the irregular network lignin, and lentinan.

(i.e., oligomers of catechin, prune juice); cf. Scheme 5 (b).^[64] Grape-seed-derived proanthocyanidine (GSP) has also been used to prepare magnetite NPs from aqueous ferric chloride solutions.^[65] Moreover, Fe₃O₄/Au hybrid NPs could be prepared by dispersing previously prepared Fe₃O₄ NPs in a solution containing chloroauric acid and, again, reduction with GSP.^[65] Proanthocyanidines are a type of polyphenol, more specifically oligomeric flavonoids, and consequently of medium to high molecular weight. Examples of other renewable reducing agents of high molecular weight that have been used without a second small-molecule reducing agent for the synthesis of metal and mixed-metal NPs include starch,^[63,66] lignin,^[67] lentinan (a polysaccharide),^[68] or chitosan (cf. Scheme 5, b).^[69] Note that all these molecules contain functions that might coordinate to metal centers (e.g., hydroxy, carboxylic acid, or ester moieties).

Metal NP syntheses using “green” reducing agents are typically carried out in water, the – without any doubt – greenest of all solvents. Water as solvent can promote the formation of (often crystalline) inorganic species when heated above its boiling point to the so-called hydrothermal regime. The following section briefly reviews the hydrothermal synthesis of inorganic materials and comments on their implementation in hybrid materials.

3.2.2. Hydrothermal Synthesis of Inorganic Materials

Hydrothermal (HT) synthesis mimics a natural ore formation process that takes place in the earth's crust. Here, subterranean streams of water circulate within delimiting rock material that does not dissolve in water. When such streams come into proximity to hot areas, such as near volcanic activity, the water is heated up, and because it is enclosed between non-dissolving rock material, autogenous pressures arise.^[70] The circulating water is, however, by no means deionized: it contains all kinds of inorganic solutes, and gases, depending on which rock materials it was in contact with and eventually dissolved.^[70] Under HT conditions, these brines can then react and often give rise to highly crystalline materials.^[71] Zeolites, for instance, are naturally exclusively formed under HT conditions.^[72] To mimic hydrothermal mineral formation in the lab, one typically employs steel tank reactors, also referred to as “hydrothermal bombs” or “autoclaves”. The use of such closed vessels generates autogenous pressures when H₂O is heated above its boiling point. There is to date no unifying definition of “hydrothermal conditions”,^[73] but the HT regime is most commonly referred to water at T above its boiling point and p above ambient pressure. When using aqueous systems above water's critical point ($T_c = 374$ °C, $p_c = 221$ bar), one would rather refer to supercritical than HT conditions. The closely related preparative technique of *solvo*thermal synthesis, with solvents other than water (e.g., ethanol, glycol) under non-ambient conditions is not discussed here.

The first synthetic HT crystallization was reported by Schafhaul in 1845, with the synthesis of small quartz crystals from *ortho*-silicic acid.^[73] A plethora of hydrothermally prepared inorganic materials (Table 1) have been reported since, including zeolites,^[72] non-zeolitic aluminosilicates,^[74] main-group- and transition-metal oxides,^[74] phosphates,^[74] chalcogenides,^[75] hydroxides,^[76] and perovskites such as CaTiO₃,^[77] BaTiO₃,^[78] BiFeO₃,^[79] and SrTiO₃.^[80] In addition, metal organic framework

(MOF),^[81] and non-framework coordination polymers^[82] are often synthesized under HT conditions. Morphology-wise, hydrothermally synthesized inorganic materials can be obtained as, for example, single crystals of impressive size (quartz, tens of cm),^[73] nano- and microparticles (BaTiO₃, PbTiO₃),^[78] or nanotubes (BaTiO₃, SrTiO₃).^[80]

The class of inorganic compounds finding the most extensive use in inorganic–organic (nano)hybrid materials is indisputably that of clay minerals. Clays are a subgroup of the phyllosilicate (or sheet silicate) family, and are layered hydrous (aluminum)silicates.^[83] As a result of their layered structures, clay minerals yield 2D colloidal objects when exfoliated. Prominent examples of phyllosilicates are kaolinite, montmorillonite, and halloysite.^[83] These clay minerals are naturally quite abundant and are mined from natural deposits.^[84] Artificial clays are sometimes preferred – mainly for their higher purity – and are synthesized hydrothermally.^[85]

From a preparative point of view, hydrothermal synthesis of inorganic compounds typically consists of the following steps. Firstly, the precursors are dispersed or dissolved in water at ambient T and p . If necessary or desired, additives are added to this dispersion/solution. These can be compounds for pH adjustment, necessary for synthesizing species that only form at a certain pH. Urea can, for instance, be used for generating basic conditions through its hydrothermal decomposition to NH₄⁺ and OH[−] ions and CO₂.^[86] Other additives that are often employed are low-molecular-weight surfactants or block-copolymers used for morphology manipulation by, for example, templating.^[74] The precursor solution is then enclosed in an autoclave and heated to the hydrothermal regime. HT reaction times range from one hour to several days, and special attention often has to be paid to cooling rates, which influence the crystallinity of the product phases. Typically, the workup is very simple: the product can be isolated through removal of the aqueous phase by decantation and is purified by subsequent washing and drying. Note that HT syntheses can also be carried out with use of microwave-assisted heating instead of conventional ovens, which reduces energy consumption through more efficient, faster heating.^[87]

Inorganic compounds prepared by HT synthesis have been applied in inorganic–organic hybrid materials. However, they were initially used with “non-green” polymeric matrices. Clay mineral particles have been extensively used for reinforcing various matrices, such as epoxy resins, polystyrene, polyethylene, and many others.^[4] In recent years, natural polymers (e.g., polysaccharides) or polymers prepared from monomers of renewable origin have become a highly active field of research. Such green polymers have indeed been combined with inorganic materials of HT origin, as discussed in detail in Sections 3.5 and 3.6. Unfortunately, the compounding procedure between inorganic D and organic M is mostly still carried out with harmful chemicals and unsafe conditions, despite the fact that a number of green polymerization techniques exist (Section 3.4).

In this section we have seen that inorganic colloids can be prepared by “green” synthetic routes, but can they also be prepared from renewable resources? Although one would typically refer to plant materials, and hence fully organic materials, as

renewable resources, a number of living species contain considerable amounts of inorganic elements that can indeed be used as precursors to inorganic materials (Section 3.3).

3.3. Inorganic Colloids from Renewable Resources

“Biom mineralization” refers to the formation of inorganic species by living organisms, including, for example, the formation of Fe_3O_4 inside magnetotactic bacteria, the formation of apatites by vertebrae, or the biosynthesis of CaCO_3 by mollusks or of SiO_2 by phytoplankton.^[41] Organisms adept at synthesizing inorganic materials are able (i) to extract inorganic elements from their surroundings (e.g., seawater for marine organisms), (ii) to accumulate these elements, and (iii) to manipulate these elements and biosynthesize inorganic materials. Consequently, one can use such organisms as sources for inorganic materials. Diatomite (i.e., sediments of dead diatoms), for instance, is commercially used for filtration materials,^[88] but can also be used as a source for inorganic materials: recently, Jing et al. have reported the use of diatomite as precursor for calcium silicate hydrate (CSH). In their approach, diatomite and $\text{Ca}(\text{OH})_2$ (slaked lime) are subjected to mild hydrothermal treatment (120–200 °C and autogenous pressure), yielding CSH after 3–72 h.^[89] The obtained CSH was mesoporous and of sponge-like to plate-like morphologies,^[89] and was further studied for water sorption.^[90] Sanhueza et al. reported the use of diatomite as raw material in the HT synthesis of the zeolites mordenite and ZSM-5, and also of ordered mesoporous SiO_2 materials of the “Mobil composition of matter” (MCM) type.^[91]

Rice husks (RHs) are another highly interesting renewable source of silica. Rice (*Oryza sativa*) accumulates silicic acid from the soil, and from this it biosynthesizes RHs (i.e., the protective shells around the rice grains, which contain ca. 20 % hydrated SiO_2 dry weight).^[92] RH is typically calcined for removal of the organic part, and consequently termed rice husk ash (RHA).^[92] Laine and co-workers have used RHA to generate silsesquioxane building blocks.^[93] In their approach, RHA was first depolymerized in methanolic choline hydroxide solution over 1–43 days at room temperature, yielding ammonium octasilicates, which were further converted into silsesquioxanes. Despite the long reaction times, it is impressive how RH, a rice industry waste product, can be used to generate nanobuilding blocks at ambient temperature. More recently, Wang et al. have used RH to prepare SiO_2 nanoparticles of narrow size distribution, as well as porous semicrystalline SiO_2 frameworks.^[94] Bansal et al. have reported an extracellular biotransformation of pristine RH (without calcination to RHA) mediated by the fungus *Fusarium oxysporum*.^[95] After only 24 h at 27 °C, quasi-spherical crystalline SiO_2 NPs of 2–6 nm were obtained – as a practical side effect, the NP surfaces were stabilized by fungal proteins.

Besides diatomite and RH, mollusk shells, which contain mainly CaCO_3 ,^[41] have been used as precursors for inorganic materials. Vecchio et al. used queen conch (*Strombus gigas*) and giant clam (*Tridacna gigas*) shells as precursors for the synthesis of biocompatible hydroxyapatite (HAp).^[96] In their approach, queen conch and giant clam shells were cut into small pieces, and subjected to HT treatment (180 °C) in $(\text{NH}_4)_2\text{HPO}_4$ solution for 2–20 days, yielding highly pure HAp that was tested as bone

implant material in mice.^[96] HAp has also been obtained by HT treatment of cuttlefish (*Sepiida*) bone, which is made of aragonite (CaCO_3).^[97] In that case, full conversion of CaCO_3 into highly porous HAp could be achieved after 48 h at 200 °C.^[97]

These few examples of inorganic materials prepared from renewable resources would all be interesting as dispersed phases in inorganic–organic hybrid materials. HAp has been extensively used as dispersed phase in polymer matrices for biomedical applications.^[98] To the best of the author’s knowledge, HAp from renewable resources has to date not been applied in these materials. Zeolites and MCM-type materials have also been used in inorganic–organic hybrid materials;^[99] also here, however, there are no examples of the preparation of such composites from inorganic dispersed phases derived from renewable resources. The aptness of inorganic materials of renewable origin for future directions in the synthesis of “fully green” hybrid materials is discussed in Section 3.6.

Up to this point, the synthesis of the inorganic component by “green” synthetic routes (Section 3.2) and from renewable resources (Section 3.3) has been reviewed. In the next sections we discuss “green” options for both origin and synthesis of the organic polymeric matrix (Sections 3.4, 3.5).

3.4. Green Polymerization Techniques

Polymer chemistry has lately been much concerned with using monomers from renewable resources (Section 3.5), but also with the development of benign polymerization techniques. This might in part be due to the omnipresence of synthetic polymers in modern daily life.^[100] This subsection does not claim completeness: we limit ourselves to enzymatic polymerization (Section 3.4.1), photopolymerization (Section 3.4.2), and hydrothermal polymerization (Section 3.4.3). Readers interested in further aspects of green polymerization techniques are referred to a recent book edited by Mathers and Meier.^[101]

3.4.1. Enzymatic Polymerization

In enzymatic polymerizations, isolated enzymes are used in vitro as biocatalysts, thus replacing conventional catalysts, which are often toxic or made up of scarce elements.^[30,102] In addition, enzymes usually function under ambient conditions, typically in aqueous environments. In living organisms, six classes of enzymes exist; of these, three have been used as biocatalysts in synthetic polymerizations (i.e., oxidoreductases, transferases, and hydrolases^[102]).

Oxidoreductases catalyze redox reactions, and this makes them apt for use in oxidative polymerizations. Several oxidoreductases have been used for the synthesis of polyaniline (PANI) under aqueous ambient conditions, which is remarkable given the fact that classical procedures involve fuming sulfuric acid.^[102a] Liu et al. reported the use of an oxidoreductase to synthesize conducting PANI–poly(styrenesulfonate) (PSS) complexes.^[103] In their procedure, PANI–PSS was obtained by polymerizing aniline at room temperature with the aid of horseradish peroxidase (HRP) in a buffered (pH \approx 4.3) aqueous solution that already contained PSS of 70000–100000 g mol⁻¹. The reaction required the presence of H_2O_2 and was complete after 1 h. PANI was also synthesized in water/dioxane mixtures by use of soybean peroxidase^[104] or of bilirubin oxidase.^[105] As

well as the monoamine aniline, aromatic diamines can be used as monomers in enzyme-aided oxidative polymerization.^[30,106] Using H₂O₂/HRP, Ichinohe et al. achieved the polymerization of *o*-, *m*-, and *p*-phenylenediamines.^[107] Another class of polymers also obtained through oxidative polymerization is that of polyphenols. These can also be obtained by applying oxidoreductases in combination with an oxidant such as H₂O₂.^[30,102a] HRP was used for the preparation of polyphenols from monophenols such as phenol and *p*-phenylphenol,^[30,108] diphenols (e.g., resorcinol, catechol) and triphenols (e.g., phloroglucinol, pyrogallol).^[109] Other enzymes used for polyphenol synthesis are laccase, soybean peroxidase, and bilirubin oxidase.^[30,110] The fact that both phenols and diamines are polymerizable enzymatically also allowed for the preparation of copolymers by use of HRP.^[111] Moreover, poly(*p*-phenylene oxide)s can also be obtained by oxidoreductase-aided polymerization with the aid of HRP, laccases, or soybean peroxidase.^[30] Here, the monomers used are derivatives of *p*-hydroxybenzoic acid (e.g., syringic acid)^[112] or 2,6-dimethylphenol.^[30] The last class of polymers that can be obtained by use of oxidoreductases is that of vinylic polymers. Thus obtained polymers include poly(acryl amide) (PAAm),^[113] poly(methacrylate)s,^[113,114] and PS.^[115]

Transferases catalyze the transfer of one functional group in a molecule to another. Phosphorylases catalyze the transfer of phosphate groups, and can be used to synthesize polysaccharides.^[116] Amylose, for instance, could be polymerized from α -D-glucose-1-phosphate and maltooligosaccharides as primers in a buffered aqueous solution with the aid of potato phosphorylase.^[117] The technique has to date been exclusively used for the preparation of amylose, but could be applied to the synthesis of an impressive number of amylose-polymer inclusion complexes, in which the second polymer was, for example, a poly-

ether, -ester, or -carbonate.^[118] With use of a glycosyltransferase, amylose could be prepared from sucrose without the need for a primer.^[119] Linear polyesters have also been prepared by use of transferases,^[102a] namely in the preparation of poly(hydroxyalkanoate)s (PHAs).^[120] Such processes are strongly biomimetic, because these polymers are synthesized by closely related mechanisms in vivo. Moreover, PHAs are of great interest as polymeric materials due to their biodegradability.^[102b]

The most widely exploited class of enzymes used in enzymatic polymerizations are hydrolases, in particular lipases.^[102] Hydrolases catalyze the cleavage of, for example, C–N or C–O bonds by the action of H₂O (or H⁺ or OH⁻). Lipases have been extensively used in the ring-opening polymerization (ROP) of lactones, yielding polyesters.^[102a] Knani et al. have reported the preparation of polyesters both from ϵ -caprolactone and from linear ω -hydroxy esters in *n*-hexane at 70 °C with the aid of porcine pancreatic lipase.^[121] Enzymatic ROP has been applied to polymerize ring sizes of four to 17, nicely illustrating the effect that reaction rates and obtained average molecular weights increase with ring size.^[122] *Candida antarctica* lipase B (CALB) has been exploited for preparing polyesters from diols and dicarboxylic acids.^[123] Other classes of polymers that can be obtained with hydrolases include: polycarbonates from diols and carbonic acid diesters,^[124] poly(amino acid)s from protease-aided polymerization of amino acid esters,^[125] polyamides from dicarboxylic acids and diamines,^[126] and poly(thioesters) from ω -mercapto-carboxylic acids or cyclic thioesters.^[127] For further information, the interested reader is directed to reviews by Heise et al.^[102a] and Kobayashi et al.,^[30,102b] in which enzymatic polymerizations are excellently covered in much detail.

As is made clear in Table 2, enzymatic polymerizations allow a wide range of polymer classes to be accessed. A few examples

Table 2. Overview of green polymerization techniques. Green polymerization techniques, the polymer classes that can be accessed with those techniques, the monomers needed, and the corresponding references are given. For typical synthetic conditions see text and cited works.

Polymerization method	Utilizable monomer	Accessible polymer	Ref. (selection)
Enzymatic polymerization with oxidoreductases (e.g., HRP, soybean peroxidase, bilirubin oxidase, laccase, chloroperoxidase, alcohol oxidase)	aniline	PANI	[103–105]
	aromatic diamines	aromatic polyamines	[30,106,107]
	phenols	polyphenols	[30,108–110]
	phenols + diamines	polyamine-polyphenol copolymers	[111]
	<i>p</i> -hydroxybenzoic acids	poly(phenylene oxide)s	[112]
Enzymatic polymerization with transferases (e.g., phosphorylases, synthases)	vinylic monomers (e.g., acryl amide, methacrylates, styrene)	polymers from vinyl polymerization (e.g., PAAm, polymethacrylates, PS)	[113–115]
	α -D-glucose-1-phosphate + maltooligosaccharide primer; sucrose	amylose	[116–119]
Enzymatic polymerization with hydrolases (e.g., lipases, proteases)	hydroxyalkanoate-coenzymes	polyhydroxyalkanoates	[102b,120]
	lactones; ω -hydroxy esters; diols + diacids;	polyesters	[121–123]
	carbonic acid diesters + diols;	polycarbonates	[102b,124]
	amino acid esters	poly(amino acid)s = poly(peptide)s	[125]
	dicarboxylic acid + diamine	polyamides	[126]
Photopolymerization	ω -mercapto-carboxylic acids; cyclic thioesters	poly(thioester)s	[127]
	vinylics (e.g., acrylates; methacrylates)	acrylic/methacrylic networks, vinylic polymers/networks	[130a]
	thiols + alkenes;	thiol-ene networks	[131]
Hydrothermal polymerization	oxiranes	epoxy networks	[132]
	dianhydride + diamine or tetracarboxylic acid + diamine	polyimides	[135,137]

in which they have been combined with renewable monomers exist (cf. Section 3.5); unfortunately there are to date no examples in which they have been applied for generating the organic matrix in hybrid materials (cf. Section 3.6).

3.4.2. Photopolymerization

Photopolymerization refers to the irreversible curing of a monomer resin through the action of photons with the aid of an appropriate photoinitiator.^[128] Because the monomer formulations used are typically solvent-free resins, and low energy input as well as low reaction temperatures are required, photopolymerization is considered a green technology.^[129] Various aspects of this topic have been extensively covered in a number of excellent reviews and books,^[128,130] to which the interested reader is directed for further reading. This review restricts itself to the brief mentioning of the polymers that can be accessed by the technique (cf. Table 2).

The most commonly used monomers in photocuring are acrylics and methacrylics, undergoing a radical photopolymerization mechanism.^[128] Photopolymerization is also used to access thiol-ene networks from multifunctional thiols and reactive alkenes.^[131] They offer several advantages over classical photopolymerization techniques, including insensitivity to oxygen.^[131] Epoxy networks can be obtained by cationic photopolymerization of multifunctional epoxy monomers.^[132] Photopolymerizations find wide application for generating polymers in biomedical applications: in dentistry, for instance.^[133] Moreover, it was recently reported, that photopolymerization can be carried out transdermally, by shining light through pig and human cadaver skin samples that had previously been subcutaneously injected with a monomer formulation, thereby laying the basis for such applications *in vivo*.^[134] In view of the strong interest in photopolymerization for biomedical materials, the technique would be highly interesting for composites in this area (compare also HAp for biomedical applications in Section 3.3).

3.4.3. Hydrothermal Polymerization

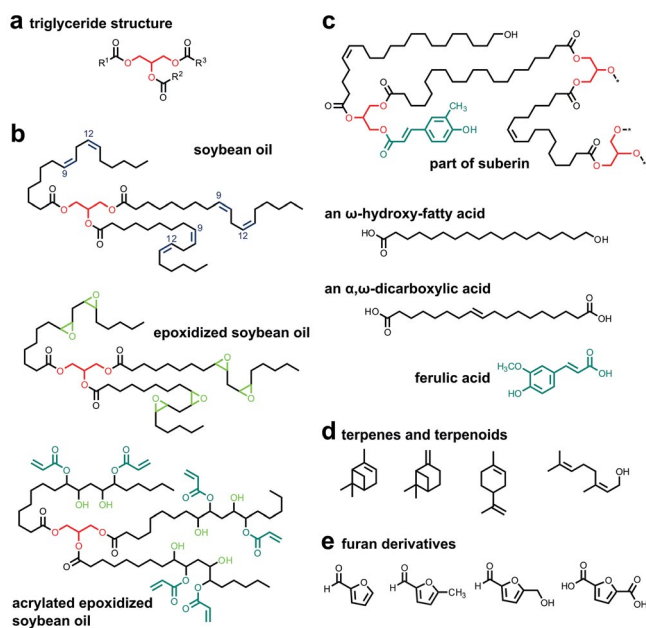
Water – the greenest of all solvents – is a most versatile environment for synthesizing inorganic materials when used under hydrothermal conditions (cf. Section 3.2.2 and Table 1). HT synthesis of inorganic compounds often yields highly crystalline materials. It has recently been shown that HT conditions can be applied for the synthesis of highly crystalline, fully condensed polyimides.^[135] These are obtained from diamine and dianhydride (or $\alpha,\alpha',\beta,\beta'$ -tetracarboxylic acid) monomers enclosed in an autoclave in water.^[135] In a first step, a monomer salt forms through an acid-base reaction between the co-monomers; this then dissolves in a stepwise fashion once the HT regime is reached, and then further forms the polyimide product by polycondensation.^[135,136] Mechanistically, the process is related to the formation of silicates from silicic acids that naturally also form by polycondensation, and is therefore referred to as “geomimetic”.^[137] The technique contrasts strongly with conventional synthetic routes to polyimides, which employ toxic, high-boiling solvents such as cresols and toxic catalysts such as isoquinoline. Moreover, classical polyimide syntheses require the continuous removal of the condensation byproduct

water (e.g., by use of Dean–Stark traps). In hydrothermal polymerization (HTP), the condensate water simply joins the surrounding H₂O while the polyimide effectively phase separates.^[135] The highly crystalline polyimide products were insoluble not only in common organic solvents but also in harsh solvents such as concentrated H₂SO₄, so average molecular weights could not be determined.^[135,136] In earlier reports, cardo-polyimides (i.e., polymers containing “loop”-shaped units in the backbone and thus displaying solubility)^[138] were synthesized by HTP.^[139] This allowed analysis of the obtained weight-average molecular weights by size-exclusion chromatography: they were up to 48000 g mol⁻¹.^[139] More recently, Kimura and co-workers have nicely combined HTP with reaction-induced polymerization at 280 °C, which led to completion of the polymerization after only 10 min.^[140] Interestingly, hydrothermal reactions have been hypothesized to play a role in the “origin of life” on earth, with studies that showed the possibility of amino acid synthesis from inorganic precursors under hydrothermal conditions,^[141] thus connecting inorganic with organic hydrothermal synthesis. In view of the plethora of inorganic species that can be formed hydrothermally, HTP would be most interesting for the simultaneous formation of inorganic and organic components of hybrid materials. As will become clear from Section 3.6, such approaches have yet to be reported.

3.5. Polymers from Renewable Resources

Living organisms are per se renewable resources. Although only small amounts of inorganic materials can be derived from renewable resources (see Section 3.3), a plethora of monomers, which can be used either directly or after facile derivatization, are found in such resources.^[142] Monomers derived from plant material include, for example, ω -hydroxy fatty acids, α,ω -dicarboxylic acids, triglycerides, phenols (derived from lignin), and terpenes (Scheme 6).^[142a,143] The polymer classes that can be built up from plant-derived monomers are briefly summarized below, as well as the applicable polymerization chemistries. For more detailed information on the topic the interested reader is referred to a number of reviews that cover the subject excellently.^[142,144] Note that numerous already polymeric organic compounds, such as polysaccharides, are found in plant materials. These are not discussed here, but their hybrid materials are examined in Section 3.6.

An important class of plant-derived monomers is that of triglyceride oils (Scheme 6, a). A triglyceride is an ester derived from glycerol and three fatty acids. The fatty acid tails typically bear reactive functions (double bonds, OH groups), and therefore polymerizable functions.^[142a] Moreover, these functions can easily be converted into other reactive groups, thus broadening the range of accessible polymer classes and polymerization chemistries. Soybean oil, for instance, is mainly composed of triglycerides of the unsaturated fatty acids linolenic, linoleic, and oleic acid (see Scheme 6, b, for a representative triglyceride). By epoxidation (e.g., with H₂O₂/HCO₂H) one obtains epoxidized soybean oil (ESO, Scheme 6, b).^[142c] Acrylated epoxidized soybean oil (AESO, Scheme 6, b) can be prepared by opening the oxirane groups in ESBO with acrylic acid, thus opening a



Scheme 6. Monomers from renewable resources. (a) General triglyceride structure. Red: glycerol-derived moiety. (b) Triglyceride-oil-derived monomers with the example of soybean oil (glycerol-derived moiety in red, alkene functions in dark blue, epoxy (middle) and hydroxy (bottom) functions in light green, acrylate groups in dark green). Top: linoleic acid triglyceride. Middle: epoxidized soybean oil. Bottom: Acrylated epoxidized soybean oil. Both depicted examples are derived from linoleic acid triglyceride. (c) Part of suberin (top) and monomers obtainable from suberin ester cleavage. Top to bottom: ω -hydroxy-fatty acids, α,ω -dicarboxylic acids, ferulic acid. (d) Three examples of polymerizable natural terpenes (left to right: α -pinene, β -pinene, limonene) and one terpenoid (geraniol). (e) Polysaccharide-derived furan monomers. Left to right: furfural, 5-methylfurfural, 5-(hydroxymethyl)furfural, furan-2,5-dicarboxylic acid.

venue for acrylate networks.^[142c] Triglycerides that find application as monomers, besides soybean oil and its derivatives, include castor, linseed, or rapeseed oil. These can be transformed into, for example, epoxy or acrylate monomers by use of the same synthetic routes as in the modification of soybean oil. Note that all these triglyceride oils are found in plant parts of high fat content (i.e., typically seeds or nuts), which are not only edible, but actually high-quality food because they provide high average physiological calorific values. Note that the use of plant material that can also be used as food products as a resource for chemical production is the subject of serious controversy.^[142b,145]

The highly abundant biopolymer suberin, mainly present in the outer bark cell walls of higher plants, is composed of aromatic and aliphatic regions.^[142a,144a] The aliphatic regions are crosslinked by glycerol esters (much as in triglyceride oils), and in addition contain ferulic acid esters (Scheme 6, c). By ester cleavage (e.g., hydrolysis or methanolysis), one obtains an aliphatic extract containing a number of difunctional monomers (Scheme 6, c): ω -hydroxy-carboxylic acids (ω -hydroxy-fatty acids) and α,ω -dicarboxylic acids, some of which contain additional functionalities within the alkyl chain (i.e., alkene, epoxy, or diol groups).^[144a]

α,ω -Dicarboxylic acids are ideal AB monomers for polyester synthesis, and α,ω -dicarboxylic acids can be used as AA mono-

mers in both polyester and polyamide synthesis. Sousa et al. reported the synthesis of polyesters from depolymerized suberin by two routes: (i) aqueous emulsion polymerization with *p*-dodecylbenzenesulfonic acid as surfactant, and (ii) enzymatic bulk polycondensation by use of CALB.^[146] The first polymerization technique is fairly gentle, being carried out in H₂O. In addition, the surfactant used is biodegradable under aerobic conditions and not considered a threat to the ecosystem.^[147] The enzymatic route used (see Section 3.4.1) is a green polymerization technique par excellence: the bulk polymerization is solvent-free and uses a bacterial (and thus renewable) enzyme as catalyst, additionally using monomers from a renewable resource that are extracted in a single-step alkaline hydrolysis. Iversen and co-workers reported an analogous lipase-mediated polymerization of an epoxy-containing ω -hydroxy-carboxylic acid that was extracted from birch suberin.^[148] More recently, semicrystalline polyesters of thermal stability up to 290 °C can be prepared from suberin extracts, again with use of benign aqueous and solvent-free polymerization techniques.^[149] In terms of their properties, the resulting macromolecular materials resemble petroleum-based aliphatic polyesters.^[144a] Monomers made from depolymerized suberin also give access to other polymer types: fatty acid monomers containing diol functions along the chain can be treated with commercial di- or triisocyanates to yield polyurethanes.^[150]

As well as triglyceride oils and suberin-derived monomers, terpenes and terpenoids (containing isoprene units but also elements other than only C and H) of natural origin have recently attracted much attention as monomers for “green polymers” (Scheme 6, d).^[144d,151] Certain terpenes are relatively abundant: orange peel extract, for instance, is >90 % D-limonene.^[152] Various polymerization chemistries are accessible, ranging from ionic, radical, or coordinative chain-growth polymerizations to step-growth polymerizations yielding polyesters, polyamides, and polyurethanes.^[144d,151] Moreover, terpenes and terpenoids are not used as energy-supplying foods, and their use as monomers thus does not compete with their use as food products. Despite this and these compounds' versatility in polymerization chemistries, there have to the best of the author's knowledge not to date been any reports on inorganic/organic nano-/colloidal composites including terpene-/terpenoid-based matrices (Section 3.6).

Lignin, one of the most abundant inedible natural polymers and a major component of trees, should be mentioned. The biopolymer has attracted much interest as a renewable resource for materials.^[142a] This is mainly due to its enormous abundance: lignin accounts for 30 % of the organic carbon on earth.^[142a,153] The structure of native lignin is highly irregular and dependent on the species from which it is isolated.^[142a] It has thus primarily been used as a filler to reinforce conventional synthetic polymers.^[142a] Approaches to depolymerization of lignin into suitable monomers with high conversion have only recently been developed.^[153,154] Rahimi et al. have presented a strategy for depolymerizing lignin most efficiently.^[153] In their approach, lignin is first oxidized, and is then depolymerized through aqueous formic acid treatment. The resulting molecules are mainly syringyl, guaiacyl, and *p*-hydroxyphenyl aro-

atics.^[153] In view of the polymerizable functions that these molecules contain (OH, OCH₃) they would be interesting as monomers, but have not to date been used as such. Note that the closely related compound syringic acid has even been polymerized into polyesters by laccase-catalyzed enzymatic polymerization (see Section 3.4.1).^[112] Consequently, lignin depolymerization products might be suited for enzymatic polymerization, even more so because the biosynthesis of lignin is enzyme-mediated.^[155] Parsell et al. reported the catalytic (Pd/C) conversion of lignin into methoxyphenols.^[154] These can be epoxidized and further polymerized, and have very recently been used as green matrix in inorganic–organic nanocomposites (see Section 3.6).^[143] Use of nickel-titanium nitride catalysts for lignin depolymerization has also recently been reported.^[156]

Furan monomers (Scheme 6, e) can readily be obtained by depolymerization of certain polysaccharides, such as xylan.^[142a,157] Whereas acid-catalyzed depolymerization of polysaccharides containing C5-glycosidic units yield furfurals (furfural or 5-methylfurfural), polysaccharides containing C6-glycosidic units are transformed into 5-(hydroxymethyl)furfural.^[142a,158] Furfurals can be transformed into other furan monomers, such as furan-2,5-dicarboxylic acid, which can then be polymerized to, for example, polyesters,^[159] or polyamides.^[142a] Note that the furan ring is a diene and can thus be applied in polymerization that proceeds through Diels–Alder reactions with dienophiles such as maleimide.^[160] As discussed in Section 3.6, furan-derived polymers have been used to a limited extent in inorganic–organic hybrid materials.

Lastly, lactic acid [i.e., 2-hydroxypropanoic acid, monomer of poly(lactic acid) (PLA)] is mentioned. The biodegradable PLA is the most important synthetic polymer derived from renewable resources.^[142a] Industrially, lactic acid is produced biotechnologically, typically by fermentation.^[156] Synthesis and applications of PLA, as well as its use as a matrix in composite materials, have been extensively covered in the literature,^[161] and are not further discussed here.

Green origins of, and synthetic routes towards, both inorganic and organic components relevant to inorganic–organic hybrid materials having been summarized, the following section (Section 3.6) is dedicated to reviewing if and to what extent these concepts have to date been implemented for “green hybrid materials”.

3.6. Hybrid Materials Based on Components of “Green” Origin or “Green” Synthesis Techniques, and Perspectives on “Fully Green” Hybrid Materials

Examples of hybrid materials that include at least one green step in their preparation or have at least one component of green origin are reviewed below. For the multitude of steps involved that can be green or not, it has been chosen to limit the considerations to four categories: (i) origin of the inorganic component, (ii) synthesis of the inorganic component, (iii) origin of the organic (polymeric) component, and (iv) synthesis of the organic matrix. Depending on how many (x) of these four categories can be viewed as green, all hybrid materials discussed in this section are termed (x|4).

In the preparation of hybrid materials, the use of inorganic compounds synthesized in green ways is certainly to be preferred to those prepared by non-benign routes. Nanoparticles – namely, metal, bimetallic, and metal oxide NPs – can be synthesized in vivo in plants, and yeast-/fungi-mediated syntheses can additionally yield metal chalcogenide NPs (Section 3.2.1 and Table 1). To date, only one (very recent) example of the use of biosynthesized NPs for the fabrication of inorganic–organic hybrid materials has been reported. This might be due to (i) research into in vivo NP synthesis now being, after an initial proof-of-concept stage, at the stage of mechanistic investigations of the formation processes and not yet at the application stage, (ii) yields of NPs obtained from organism-mediated synthesis being extremely small, which is certainly hampering their applicability to the field of hybrid materials, and/or (iii) extraction of biogenic NPs being tedious and involving a high risk of destroying the nanostructures. A most elegant example of green synthesis of biosynthesized Pd NPs and further conversion into an inorganic–organic hybrid material has recently been reported by Clark and co-workers.^[53] The authors synthesized these Pd NPs in thale cress (*Arabidopsis thaliana*), in only 24 h under ambient conditions, by liquid culture from aqueous K₂PdCl₄ solutions. From t₀ to t = 24 h the thale cress plants turned brown and wilted, and contained well dispersed, spherical Pd NPs from ca. 3 nm (after 3 h) to up to 32 nm in diameter (after 24 h), as demonstrated by transmission electron microscopy (TEM) of the corresponding samples (Figure 1). After Pd NP biosynthesis, the plant material was washed, ground, dried, and heated to either 300 or 800 °C. The material pyrolyzed at 300 °C consisted of 15 wt.-% Pd and 85 wt.-% C and O, and so can be understood as a hybrid material of supported NPs. Due to the relatively low pyrolysis temperature (300 °C), the obtained organic matrix can be qualified as organic carbon material. These materials were shown to display impressive catalytic activity in Suzuki–Myaura coupling of aryl halides with phenylboronic acids (e.g., >98 % yield for aryl chlorides). Interestingly, the supported Pd NPs obtained by pyrolysis at 800 °C were less catalytically active, and aggregation of the NPs was observed.^[53] Overall the biogenic supported Pd particles are a nice example of a 3|4 green hybrid.

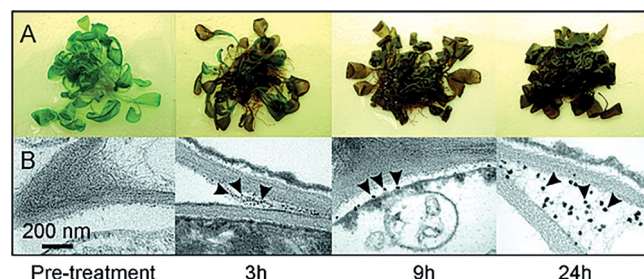


Figure 1. Pd uptake and Pd NP formation in *Arabidopsis thaliana*. A: Appearance of 3-week-old plants 0–24 h after treatment with K₂PdCl₄. B: TEM images corresponding to photographs in A, illustrating Pd NP accumulation and increase in size over time. Figure reproduced from ref.^[53] published under the Creative Commons Attribution (CC BY) license.

Note that in addition to catalytic activity found for several metal NPs, the types of inorganic materials that can be synthe-

sized in vivo show other interesting physicochemical properties that have already been investigated as dispersed phases in hybrid materials. The photothermal effect in Au NPs, for instance, was elegantly used for in situ heating in Au NP/poly(acrylonitrile) nanocomposites,^[162] and the magneto-optical properties of magnetite NPs were shown to persist when embedded in a poly(methyl methacrylate) matrix.^[163]

For ex vivo organism-mediated NP syntheses, yields were not given in the articles discussed in Section 3.2.1,^[40,48–50,52,58–60] but they are also supposed to be quite small. Ex vivo, SiO₂, TiO₂, and BiTO₃ NPs could be obtained in addition to metal and bimetallic particles synthesized in vivo. These inorganic NPs have already been shown to be highly interesting for use in hybrid materials. For instance, TiO₂-polymer nanocomposites have been reported to show antimicrobial effects,^[164] or to exhibit enhanced electrical energy density.^[165] Although a small number of inorganic-inorganic hybrid materials based on inorganic NPs from ex vivo biosynthesis exist,^[166] such NPs have to the author's best knowledge not to date been used in inorganic-organic hybrid materials.

NPs synthesized by use of benign reducing agents [i.e., either low-molecular-weight (e.g., vitamin C, glucose),^[61–64] or high-molecular weight (e.g., polysaccharides), Section 3.2.1, Table 1] are potent alternatives to conventional reducing agents (e.g., NaBH₄ or hydrazine). The use of small-molecule reducing agents offers great potential because they are chemically pure, which increases control over obtained particle sizes and shapes in relation to use of plant extracts. Espuche and co-workers very recently reported the use of glucose as reducing agent for the preparation of Ag/starch composites.^[167] Because starch is a polymer of renewable origin, and the dispersed NPs were prepared in a green, water-based way, this is a nice example of a highly green approach. In a follow-up the authors combined this approach with the addition of montmorillonite particles, which are also "green" because they are produced hydrothermally. With or without montmorillonite, both reported hybrid materials are 3|4 green hybrids. Depending on the exact preparation, Ag NPs and the silicate filler showed synergistic effects on dispersibility in the starch matrix and oxygen barrier properties.^[168]

Natural polymeric reducing agents, such as polyphenols, starch, lignin, lentinan, or chitosan,^[65–69] are most intriguing. As briefly mentioned above (Section 3.5), certain biopolymers, especially polysaccharides, can be used as matrix materials, either directly or after slight derivatization [e.g., chitosan (cf. Scheme 5, b) is produced by deacetylation of natural chitin). They are typically investigated as materials for structural applications, and combination with inorganic components is thus primarily directed towards mechanical reinforcement. This is achieved by fabricating either colloidal fiber-reinforced (e.g., carbon/silicon nanotubes) or 2D-colloid reinforced (typically clay) polysaccharide composites. However, also of interest is the biodegradability of polysaccharides (further discussed at the end of Section 3.6). In combination with metal NPs, nanohybrids with intriguing properties could be fabricated (e.g., Au/chitosan hybrids have been used with respect to antioxidant properties,^[169] as electrochemical sensors,^[170] or as substrates

for surface-enhanced Raman scattering^[171]). In some examples of Au NP/chitosan fabrication, NaBH₄ is still used for reducing HAuCl₄. Recently, the double use of chitosan both as reducing agent and as matrix is finding application, as excellently implemented by Aroca and co-workers.^[171] Ag NP/starch hybrids show potential as antimicrobial biodegradable hybrids.^[172] Starch was used as dual reagent (i.e., as reducing and as stabilizing agent for Ag NPs) by El-Rafie et al.,^[173] although the polymer here is a surfactant rather than a major component (as in the case of a matrix). White et al. reported the synthesis of Ag NPs of 5–25 nm in mesoporous starch, together with the use of the resulting composites as antimicrobial materials.^[174] Their synthetic approach is very benign: a mesoporous starch hydrogel was infiltrated with AgNO₃ and left to stir for 15 h at room temperature, followed by solvent exchange of water for ethanol and drying. Here, the starch fulfils the roles of reducing agent, NP stabilizer, and NP support in the final hybrid material.^[174] An earlier report by the same group presents the preparation of Pd NPs supported on mesoporous starch and their applicability as catalyst systems in cross-coupling reactions.^[175] Here, the Pd NPs were also synthesized by simply adding a palladium acetate solution to the starch hydrogel and subsequent solvent extraction and drying. The obtained starch-supported NPs were shown to be highly efficient in Heck, Suzuki, and Sonogashira reactions, and, most impressively, to be reusable. The significant catalytic properties were in part attributed to the highly porous structure of the mesoporous starch.^[175,176] Recently, alginic acid and seaweed have been added to the list of biopolymer supports for metal NPs.^[177] All of these examples qualify nicely as 3|4 green hybrid materials. However, there is still a broad range of biopolymers that are potentially interesting for their potential dual roles both as reducing agent and as support. For instance, to the author's best knowledge there are to date no reports on cellulose/metal NP nanohybrids with cellulose used both as matrix and as reducing agent.

Hydrothermal synthesis can be used to obtain a plethora of inorganic materials, ranging from metal oxides, phosphates, chalcogenides, and coordination polymers to silicates (cf. Section 3.2.2 and Table 1). In particular, clay minerals, which are mostly phyllosilicates, are widely used as dispersed phases in inorganic-organic hybrid materials, typically for enhancing mechanical or barrier properties.^[4] Even commercial clays are of either natural or synthetic hydrothermal origin.^[84] Thus they can be considered a "green" component in hybrid materials. In addition, inorganic colloids can be prepared from renewable resources to a limited extent [i.e., restricted to elements found in biomineralized structures (mainly Ca, Si, C, S, O), Section 3.3]. Mollusk shells and cuttlefish bone were shown to be convertible into HAP,^[96,97] which is indeed a material of interest in composites for biomedical applications. Moreover, zeolites and mesoporous silica could be prepared from diatomite,^[91] which is derived from diatoms and thus renewable. All examples of renewables-derived inorganic compounds are prepared by the green route of hydrothermal synthesis. However, none of these examples has to date been used in inorganic-organic hybrid materials. The recently developed technique of hydrothermal polymerization operates under the same *T*- and *p*-conditions as

inorganic hydrothermal syntheses.^[135–137,139] Consequently, it might even be possible to combine the synthesis of inorganic and polymeric components hydrothermally in one single step. Such combined approaches have not to date been reported; this might be related to the fact that HTP is a new technique and to date limited to one class of polymers (i.e., polyimides).

Enzymatic polymerization (Section 3.4.1) is a green technique that can be used for a broad range of polymer classes (Table 2). Apart from the fact that enzymes are renewable, the route benefits from the conditions under which most enzymes operate (i.e., aqueous, ambient conditions). Although enzymatic polymerization have already been used to polymerize monomers from renewable resources (specifically from suberin, Section 3.5), the technique has yet to be applied to the synthesis of inorganic–organic hybrid materials.

Photopolymerization (Section 3.4.2 and Table 2) is benign in terms of often solvent-free formulations, low energetic requirements, fast polymerization processes, and low T and p . With two-photon polymerization (2PP), rapid prototyping can be achieved with impressively high spatial resolution.^[178] For the fabrication of inorganic–organic hybrid materials, combined sol-gel and 2PP approaches have been reported.^[179] These approaches use hybrid precursors that combine vinylic moieties for photopolymerization and alkoxide moieties for sol-gel reactions, thus leading to class II hybrid materials. In combination with presynthesized inorganic colloids, photopolymerization has also been reported. For dental applications, acrylic resins containing SiO₂ particles as filler are photopolymerized.^[180] Photopolymerization of epoxy monomers by a cationic mechanism has been applied to the synthesis of inorganic–organic hybrid materials, with the inorganic components being Fe₂O₃,^[181] TiO₂,^[182] and SiO₂.^[183] Most recently, a few elegant examples of the combination of photopolymerization with monomers from renewable resources for composite materials have been reported. Syntheses of hybrid materials with matrices from renewable resources are discussed in detail in the following paragraph.

Polymers based on renewable triglyceride oil monomers (e.g., soybean, linseed, or castor oils in their epoxidized or acrylated forms) are certainly most commonly used for hybrid materials. Interestingly, this arose from a mere necessity: the aliphatic chains in natural triglycerides are derived from fatty acids of considerable length (typically six to 21 carbon atoms), which thus generates significant molecular flexibility. Consequently, these polymers often do not provide sufficient rigidity and strength for structural applications.^[184] Through the preparation of nanocomposites, the mechanical properties of such polymers from renewable resources could be much enhanced. Note that numerous macroscopic composite materials, with fillers such as glass, carbon, aramid, or natural fibers, in matrices from renewable resources have been reported.^[185] The interested reader is referred to recent reviews covering this topic.^[185,186] Kobayashi and co-workers reported an early example of a combination of a green dispersed phase, natural clay, in a green matrix, an epoxy resin prepared from ESO.^[184] Organophilic octadecyl-modified montmorillonite (OMM) was in-

tercalated with ESO, and the mixture was then thermally cured at 150 °C with use of a benzylium hexafluoroantimonate latent catalyst. Depending on the clay content, the silicate layers of the clay were either fully exfoliated (randomly oriented, for 5 wt.-% clay), thus leading to a 2D colloid, or intercalated (with structural ordering, for >10 wt.-% clay). Whereas the pure epoxy resin prepared for comparison resulted in a rather soft film, the OMM/ESO nanocomposite produced mechanically stable, flexible films. Both dispersed phase and matrix can be categorized as green. However, fabrication of the composite requires curing at relatively high temperatures (150 °C) and the use of the benzylium hexafluoroantimonate catalyst. Hexafluoroantimonate salts have been shown to be highly toxic to green algae.^[22] The paper gives no information on the amount of the “catalyst” used, but such initiators for polymerization of epoxy resins are sometimes used in amounts of several wt.-%.^[187] Despite the non-green polymerization technique, this report is nicely close to a fully green hybrid material, with 3|4 according to our previously defined scale.

Lligadas et al. have used epoxidized linseed oil (ELO) as matrix for nanocomposites.^[188] Commercial functionalized polyhedral oligomeric silsesquioxane (POSS) was dispersed in ELO and thermally cured at temperatures of 140 °C, 170 °C, or 190 °C in the presence of *N*-benzylpyrazinium hexafluoroantimonate as latent catalyst. Prior to thermal curing, the preparation involved the dispersion of POSS in acetone and the compatibilization of this mixture with ELO for 2 h, followed by removal of the solvent by application of reduced pressure. The obtained nanocomposites showed higher T_g values and storage moduli than the unreinforced resin prepared for comparison. The obtained nanocomposites were nicely homogeneous: below 2 wt.-% POSS loading no aggregation of POSS was observed, whereas higher loading led to uniformly dispersed spherical aggregates of up to 150 nm in diameter. Although ELO is derived from a renewable resource, POSS cages are conventionally synthesized by scarce-water hydrolysis and condensation of chloro- and alkoxy silanes in organic solvents.^[189] Thus, they do not qualify as a green dispersed phase. Compatibilization of D and M required the use of organic solvent (acetone), and curing was performed in the presence of a pyrazinium hexafluoroantimonate at elevated temperatures, as in the synthesis of OMM/ESO nanocomposites. Hence, the obtained hybrid material qualifies as 1|4 green hybrid.

More recently, ESO-based epoxy resins have been reinforced with TiO₂^[190] and with ZnO.^[191] Sithique achieved TiO₂ reinforcement by copolymerizing a 30:70 wt.-% mixture of ESO with the diglycidyl ether of bisphenol A (DGEBA) with 4,4'-diaminodiphenylmethane (DDM) in the presence of TiO₂ nanoparticles (anatase, 1, 2, 3, and 7 wt.-% loading). Curing was carried out by a two-step temperature profile (3 h at 120 °C followed by 2 h at 180 °C). The prepared nanocomposites displayed enhanced tensile strength and T_g values (relative to the unreinforced epoxy resin prepared for comparison). Despite the absence of a curing catalyst, the synthesis cannot be qualified as green. Firstly, the ESO content (30 wt.-% with respect to DGEBA) was quite low, and secondly the co-monomers DGEBA and DDM were used.

The reinforcement of ESO with ZnO nanoparticles reported by Díez-Pasqual and Díez-Vicente showed impressive improvements in mechanical properties (Young's modulus, tensile strength, hardness), thermal properties (T_g , heat distortion temperature), barrier properties (reduced water absorption and gas permeability), and antibacterial properties.^[191] The synthesis was performed by curing a dispersion of ZnO in ESO in the presence of 4-(dimethylamino)pyridine (DMAP) as latent catalyst (3 wt.-%) at 120 °C overnight. No co-monomer besides ESO was used, and the curing temperature is, at 120 °C, rather low for an epoxy system. However, DMAP is toxic, and overall the hybrid material is a 1|4 green hybrid.

The epoxy moieties in epoxidized seed oils can be converted into, for example, acrylates, which gives access to a plethora of other polymerization chemistries. Acrylated ELO (AELO) was reinforced with TiO₂ NPs, giving rise to antimicrobial nanocomposites.^[192] Synthesis-wise, the formulations used contained AELO, the crosslinking co-monomer 2,2-bis[(methacryloyloxy)methyl]butyl methacrylate, benzophenone as photoinitiator, and 2-(dimethylamino)ethanol as coinitiator. These were mixed with TiO₂ nanoparticles, cast as thin films onto glass plates, and photopolymerized by use of UV lamps. This is indeed a nice example of combining monomers from renewable resources with a green polymerization technique for the preparation of hybrid materials: in sum a 2|4 green hybrid. Note that neither co-monomer nor photoinitiator nor coinitiator used in this formulation are toxic.

AESO has been used as matrix with CNTs and CNT/soot mixtures as nanofillers.^[193] For reinforcement with CNTs (up to 3 wt.-% loading), AESO was thermally copolymerized with styrene (Sty, weight ratio AESO/Sty 65:35) with use of 1.5 wt.-% *tert*-butyl peroxybenzoate as radical initiator. The applied temperature protocol was 2 h at 110 °C followed by postcuring at 180 °C for 2 h.^[193a] A considerable improvement in the nanocomposite materials' mechanical properties relative to the AESO/Sty resin prepared for comparison was observed for low CNT loadings. However, the mechanical properties deteriorated at higher loading, which was attributed to CNT agglomeration. Analogous procedures were used for CNT/soot as filler.^[193b] The synthesis requires Sty as co-monomer and is carried out at relatively high temperatures, but for short reaction times.

Acrylated castor oil (ACO) has been used by Luo et al. to prepare a nanohybrid.^[194] They generated POSS-reinforcement by "thiol-ene" photocuring of ACO in the presence of thiol-terminated POSS. The obtained homogeneous transparent nanohybrid films showed improved thermal properties, but a decrease in mechanical performance (Young's modulus and hardness), which was related to the high loadings in POSS (smallest loading was 25 mol-%, highest loading 150 mol-%). The photopolymerization of an equimolar POSS/ACO mixture was complete after only 240 s, and did not require any additives. This short reaction time nicely illustrates the low energy input required by photopolymerization, and the prepared hybrid material is a 2|4 green hybrid. Castor oil (CO) can also be used in other polymerization chemistries. Recently, CO was used to prepare nanocomposites in polyurethane (PU) matrices reinforced with either montmorillonite^[195] or silica.^[196] For silica incorpora-

tion, CO was converted into an alkoxy silane CO (ASCO) precursor by acid-termination with succinic anhydride and further functionalization to ASCO with [3-(glycidyoxy)propyl]trimethoxysilane.^[196] Firstly, a prepolymer was prepared by treating ASCO with isophorone diisocyanate (IPDI) and dibutyltin dilaurate (DBTDL) as catalyst at 70–80 °C. The prepolymers were then cast as films and subjected to atmospheric moisture for 40 days, thereby allowing moisture curing of the PU and hydrolysis and condensation of the alkoxy silane moieties to silica. The ASCO-based PU films showed better mechanical and viscoelastic properties than the unmodified CO-based PU prepared for comparison. Montmorillonite/CO-based PU was carried out by an analogous procedure: CO was treated with IPDI, DBTDL and 2,2-bis(hydroxymethyl)propionic acid to afford a prepolymer that was converted into the final nanocomposite in the presence of montmorillonite by the addition of water.^[195] Although carried out under ambient aqueous conditions, in both cases, the preparation of the prepolymer involved the use of the non-toxic IPDI, and the organotin compound DBTDL as catalyst. Organotin compounds are generally toxic and detrimental to the environment, especially to aquatic ecosystems.^[197] Overall, these two approaches are hence 3|4 green hybrid materials.

Monomers from lignin depolymerization were recently used for preparing hybrid materials. This is nicely complementary to the conventional use of lignin as filler to reinforce conventional polymers.^[142a] Approaches to depolymerization of lignin into suitable monomers with high levels of conversion have only recently been achieved^[153,154] (see Section 3.5). Zhao and Abu-Omar recently reported the use of dihydroeugenol (DHE, 2-methoxy-4-propylphenol) as starting point for montmorillonite-reinforced nanocomposites.^[143] DHE is one of the major products of the catalytic conversion of lignin into methoxyphenols over Pd/Zn/C.^[154] The methoxy group in DHE could be converted into a hydroxy group, and a diepoxy monomer was produced upon glycidylation with epichlorohydrin. The nanocomposite was obtained by copolymerizing the epoxy monomer with diethylene triamine (DETA) in the presence of 3–12 wt.-% OMM. Better mechanical and thermal performance could be achieved than in the case of a pristine epoxy-amino network. The synthesis of the nanocomposite did not require any additives or catalysts and was carried out at impressively low temperatures (i.e., by subsequent heating to 30, 65, and 90 °C, for 2 h each). Overall the obtained material qualifies as a 4|4 green hybrid.

Monomers from suberin depolymerization (i.e., various ω -hydroxy-carboxylic acids, α,ω -dicarboxylic acids, and ferulic acid (Section 3.5) are promising candidates for hybrid materials. These monomers can be obtained by straightforward ester cleavage, and they were even shown to be polymerizable through a green, enzymatic polymerization process.^[146,148,149] Moreover, the properties of, for example, polyesters derived from these monomers have been reported to be comparable with those of synthetic polyesters.^[142a,144a] Nonetheless, to date there are no studies reporting their reinforcement with inorganic dispersed phases, either nano- or micron-sized. It is the author's belief that these polymers from renewable resources – especially when green polymerization techniques are used –

could be ideal candidates for the fabrication of fully green inorganic–organic composites.

Terpenes can be polymerized to give various types of polymers (see Section 3.5 and Table 2).^[144d,151a] As matrix materials in composites, they have found only little application to date. Ando et al. reported the preparation of class II hybrids from copolymerization of methacryl-terminated POSS with limonene and pinene diacrylates through photocuring.^[198] The approach combines photopolymerization with the use of monomers from renewable resources (that are, however, derivatized to acrylates). Despite the derivatization, the approach yields a highly green 2|4 hybrid material, with POSS and its synthesis being of non-green origin. Other terpene-based inorganic–organic hybrid materials are yet to be reported.

Furans can be generated from poly- or monosaccharides (see Section 3.5).^[142a,157] They can be treated to provide, for example, polyamides or -esters, and their dienic character can also be used for polymerization through Diels–Alder reactions. Monti et al. recently reported the preparation of poly(furfuryl alcohol)–SiO₂ NP composites by use of commercial Ludox® suspensions and poly(furfuryl alcohol) prepolymers.^[199] By use of amino- or isocyanatosilanes, SiO₂ NPs with free –NH₂/–OCN surface functionality can be generated. These surface-functionalized SiO₂ NPs are able to crosslink with the prepolymer. By stirring a mixture of the prepolymers with surface-functionalized SiO₂ NPs at room temp. overnight and subsequent 2 h of curing – rather mild conditions – class II hybrid materials could be obtained. The synthesized hybrids showed improved fire resistance and mechanical stability relative to the pristine resins.^[199] overall a 2|4 green hybrid. Rivero et al. reported the preparation of a montmorillonite-reinforced phenolic resin, obtained by copolymerizing phenol with furfural in aqueous K₂CO₃ at 150 °C in the presence of commercial montmorillonite clays.^[200] This is an example of the replacement of formaldehyde in phenol-formaldehyde resins by furfural. Nonetheless, the co-monomer phenol is toxic, and the approach thus yields a 3|4 green hybrid.

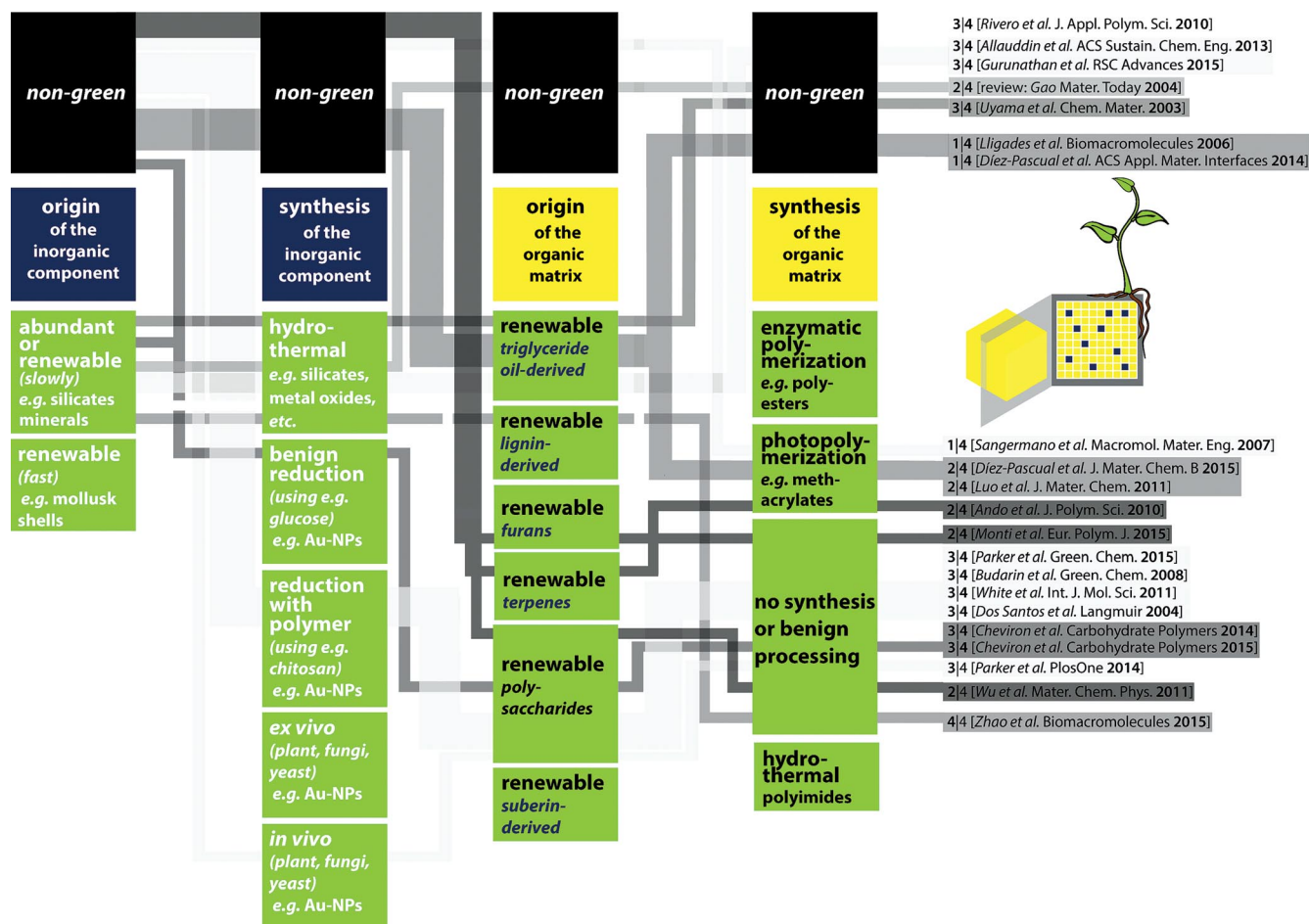
Polysaccharides as matrix represent a contrast to forming the organic matrix from monomers of natural origin (Section 3.5 and Table 2). Examples of their use in hybrid materials include, for example, cellulose, chitin, chitosan, or starch with nanotubes [e.g., CNTs, silicon, or hallyosite nanotubes (HNTs)].^[201] This research field was recently reviewed by Liu, Chang, and co-workers.^[201] Whereas HNTs are readily dispersible, due to their charged surfaces, pristine CNTs are challenging to disperse.^[201] To generate dispersibility they can be covalently linked to the polymeric matrix, but chemical modification of the CNTs is needed. This requires harsh routes with, for example, HNO₃/H₂SO₄,^[201] elemental F₂ at 150–600 °C,^[202] ozonolysis,^[203] or the use of diazonium salts.^[204] Generally, the functionalization of CNTs and their covalent linking to the polymer matrix yields excellent mechanical properties: in particular, outstanding stress-strain transfer between nanotubes and the polymer matrix.^[201] However, CNT functionalization disrupts the delocalization, thus hampering the conductivity of these nanocomposites.^[201] As well as covalent functionalization, noncovalent interactions can be used to disperse CNTs. Low-molecular-weight compounds that adhere to CNTs through π – π interactions are

typically aromatic, such as pyrene-carrying surfactants,^[202b] or benzyl alcohol.^[9] Other means of noncovalent functionalization include the use of surfactants such as sodium dodecylsulfate, and also the use of chain-flexible polymers that physically interact with the CNT by “wrapping” around it.^[205] From a green chemistry perspective, noncovalent functionalization is to be preferred: it clearly applies less harsh conditions than covalent functionalization, and also uses fewer derivatization steps. Barrau et al. reported an elegant example in which reinforcement of an epoxy matrix with CNTs was achieved by use of palmitic acid as an amphiphile.^[206] Palmitic acid is an extremely common fatty acid in animals and plants and thus in renewable sources. This noncovalent functionalization allowed electronically intact CNTs to be used, and nanocomposites exhibiting excellent electrical conductivity could be prepared.^[206] For reinforcement of polysaccharide matrices with CNTs, the CNTs are, unfortunately, chemically modified by the harsh protocols listed above, which yields covalent linking and thus class II hybrids.^[201] Recently, one example of polysaccharide reinforcement with CNTs based on noncovalent interactions, was reported by Li and co-workers,^[207] who used a hydrophilic–hydrophobic block copolymer as surfactant and obtained a CNT/chitosan class I nanohybrid by simple mixing of aqueous solutions and subsequent evaporation of water.^[207] Despite the ease of preparation, great dispersibility and enhanced mechanical properties were obtained. The prepared material qualifies as a 2|4 green hybrid. For the dual use of polysaccharides as reducing agent and matrix in nanohybrids of metal nanoparticles, see “natural polymeric reducing agents” (earlier in this section).

3.7. Perspectives for the Green Synthesis of Inorganic–Organic Hybrid Materials

The fact that inorganic–organic hybrid materials have at least two different components gives rise to a number of points, relating both to origin and to fabrication steps, that can be green or not. This review aims at globally summarizing green syntheses of the inorganic and organic components, in terms both of their origin and of their preparation. Section 3.6 analyzes if and to what extent these components have already been implemented for hybrid materials with the dispersed phase in the colloidal domain. Therefore, a scale to qualify how green a hybrid material is has been used, in which four categories are analyzed: (i) origin of the inorganic component, (ii) synthesis of the inorganic component, (iii) origin of the organic matrix, and (iv) synthesis of the organic matrix. The author is not claiming completeness and might have overlooked further examples, but it is clear from Section 3.6 there is still a lot of room to explore and for improvement. To visualize all routes that should and can still be exploited or fortified, preparations of components discussed here are summarized in the form of a type of map in Scheme 7.

Please note that only the topics reviewed here are depicted in Scheme 7. Because “non-green” techniques and origins were not the direct subject, these are depicted as black areas without further specifications (Scheme 7). Note that two pairs of “green” steps have already been combined, but have yet to be applied



Scheme 7. Map of green synthesis of inorganic–organic hybrid materials. Illustration of the points in which regard a binary inorganic–organic hybrid material can be “green”, with use of the categories discussed in this review (i.e., origin of the inorganic component, synthesis of the inorganic component, origin of the organic polymeric component, and synthesis of the organic polymeric component). Refs. for examples are given in the scheme (from top to bottom: refs. [200,196,195,4,184,188,191,181,192,194,198,199,177,175,174,171,167a,167b,53,207,143])

to the synthesis of hybrid materials: inorganic colloids have been prepared from renewable resources through hydrothermal techniques, and renewable-derived polymers have been generated through enzymatic polymerization. The connections in Scheme 7 illustrate pathways that have been reported (for precise examples, see in particular Section 3.6). Here it is noteworthy that most reported syntheses pass through “non-green” (black boxes, top of Scheme 7) at some point. Moreover, it is clear that the interest in this topic is quite recent: all references given in Scheme 7 are no older than 10 years. Strikingly, the use of monomers from renewable resources does often not go hand in hand with benign polymerization techniques or “green” inorganic colloids. The combination of as many “green” components and synthesis steps as possible remains an open challenge and leaves much room for synthetic creativity.

4. Conclusion

This article has reviewed the green synthesis of inorganic–organic hybrid materials involving inorganic phases as the minor component in organic polymer phases as the major compo-

nent. In order to cover this topic, the green approaches to both components were first analyzed separately. It has become clear that there are several interesting benign routes towards inorganic colloids (hydrothermal synthesis, organism-assisted synthesis), and that they can even be generated from renewable resources. Organic polymers can also be prepared from renewable resources and polymerized by green routes. Nonetheless, all these techniques are only rarely combined in one, leaving a lot of room for innovative hybrid materials synthesis.

Keywords: Green chemistry · Renewable resources · Inorganic-organic hybrid materials · Composites · Polymers

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