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Biomimetic Materials in Our World: A Review.

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Abstract: *The study of biomineralization offers valuable and incredible insights into the scope and nature of material chemistry at the inorganic and organic surfaces. Biological systems (architecture) are replete with examples of organic supramolecular assemblies (double and triplet helices, multisubunit proteins, membrane-bound reaction centres, vesicle, tubules e. t. c.), some of which (collagen, cellulose and chitin) extend to microscopic dimensions in the form of hierarchical structure, There are ample opportunities of lessons from the biological (on growth and functional adaptation), and physical (properties and compositions) world. This review explores the field of biomimetic material chemistry as it relates to fibres with respect to their historical perspective, the use of the products of biomimetic material, the progressive efforts and a general overview. Conclusively, biomimetic materials research is indeed a rapidly growing and enormously promising field that needs to be explored.*
Key words: *Biomineralization, helices, material chemistry, nature, supramolecular.*

I. Introduction

The natural world around us provides excellent examples of functional systems built with a handful of materials. Throughout the millennia, nature has evolved to adapt and develop highly sophisticated methods to solve problems [1]. There are numerous examples of functional surfaces, fibrous structures, structural colours, self-healing, thermal insulation, etc., which offer important lessons for the fibre products of the future. Biomimetic research is a rapidly growing field and its true potential in the development of new and sustainable fibre can only be realized through interdisciplinary research rooted in a holistic understanding of nature.

The material design mimics the structural concepts of the dermis of sea cucumbers. These creatures feature soft connective tissue with mutable mechanical properties; the animal can switch between low and high stiffness within seconds. To realize this effect, nature relies on a nanocomposite in which collagen fibrils reinforce a low-modulus matrix. A regulatory protein varies the degree of binding and stress transfer between adjacent fibrils to control the macroscopic properties of the system.

Animals, plants and insects in nature have evolved over billions of years to develop more efficient solutions, such as superhydrophobicity, self cleaning, self repair, energy conservation, drag reduction, dry adhesion, adaptive growth and so on, than comparable man-made solutions to date [2]. Some of these solutions may have inspired humans to achieve outstanding outcomes. For example, the idea of fishing nets may have originated from spider webs; the strength and stiffness of the hexagonal honeycomb may have led to its adoption for use in lightweight structures in airplane and in many other applications.

Although the science of biomimetics has gained popularity relatively recently, the idea has been in existence for thousands of years. Since the Chinese attempted to make artificial silk over 3000 years ago, there have been many examples of humans learning from nature to design new materials and devices. Leonardo da Vinci, for example, designed ships and planes by looking at fish and birds, respectively [3]. The Wright brothers designed a successful airplane only after realizing that birds do not flap their wings continuously; rather they glide on air currents [3].

Engineer Carl Culmann in 1866, while visiting the dissecting room of anatomist Hermann Von Meyer, discovered striking similarity between the lines of stresses (tension and compression lines) in a loaded crane-head and the anatomical arrangement of bony trabeculae in the head of a human femur. In other words, nature has strengthened the bone precisely in a manner dictated by modern engineering [4]. Arguably, one of the most well-known examples of biomimetics is a textile product. According to the story, George de Mestral, the Swiss inventor went for a walk in the field with his dog. Upon his return, he noticed burrs stuck to his trousers and to his dog's fur. Upon closer inspection of the burrs, de Mestral discovered their hook-like construction, which led to his invention of the hook and loop fastener, Velcro (http://www.velcro.com/index.php?page=company).

There are many more examples of inventions drawing their inspiration from biological systems. This review explores the field of biomimetics as it relates to fibres. The exploration begins with a general overview, followed by a historical perspective; it describes some ongoing efforts in biomimetic materials. Finally, it explores the potential use of biomimetic materials and products towards the attainment of sustainable fibres. In general, the aim is not to emulate a particular biological architecture or system but to use such knowledge as a source of guiding principles and ideas. The underlying philosophy is therefore based on what might be termed as “soft interpretation”, along with a large element of imagination [5]. By combining known technologies such as lithography or surface probe microscopies [6-7]. and complex functions or recognition abilities of biological systems, [8-9] micro and nanometer-scale architectures that integrate features such as anisotropy [10-11] specific binding [12-15] or motion [16-19] have been designed for potential applications in active nanodevices [20-24] dealing with electronic information and mechanical tasks, pre-encoded surface coatings for clinical testing and screening, structure-function elucidation, and new interface probes.

However, the interest here is in how these organic architectures can be associated with inorganic solids to give unique and exquisite biominerals, e. g. diatom frustules, coccoliths, seashells, bone, e.t.c.in which the structure, size, shape, orientation, texture and assembly of the mineral constituents are precisely controlled [25]. For numerous numbers of scientists, bioinorganic materials represent a source of inspiration for material synthesis. In fact, what actually captured the imagination is how such relatively simple inorganic material such as $CaCO_3$, SiO_2, Fe_3SO_4, etc can be formed into precise functional architectures which include tough, durable and adaptive polymer-ceramic composites which can be fabricated using calcium phosphate and calcium carbonate by organized assembly based on specific molecular interaction [26]. If these biological archetypes can be reformulated in a synthetic context then perhaps the biomimetic design of nano- microscale materials and composites based on inorganic materials could be a real possibility in future processing strategies

The main thrust in the area of biomimetic/bio-inspired materials is the exploration of a radically new approach for the design of bio-inspired, synthetic polymers with stimuli-responsive mechanical properties. Materials, in which an external stimulus causes a reversible change of the mechanical properties, are the target. This functionality can oftentimes be exploited in various material platforms, which have the potential to enable applications that range from biomedical implants to robotic elements to adapting protective clothing to orthopaedic devices with controllable characteristics.

II. Definition of Biomimetic material

Biomimetic materials are materials developed using inspiration from nature. This may be useful in the design of composite materials, or material structures. Natural structures have evolved many inspiring examples that have been used by man. Common examples are the honeycomb structure of the beehive, the fibre structure of wood, spider silks, nacre, bone, hedgehog quills.

Biomimetic is the examination of nature, its models, systems, processes, and elements to emulate or take inspiration from in order to solve human problems [27]. Similar terms include bionics [28]. The term ‘biomimicry’, or imitation of nature, has been defined as, ‘copying or adaptation or derivation from biology’ [29]. The term ‘bionics’ was first introduced in 1960 by Steele [30] as, ‘the science of systems which has some function copied from nature, or which represents characteristics of natural systems or their analogues’. The term ‘biomimetics’ introduced by Schmitt [31] is derived from bios, meaning life (Greek) and mimesis, meaning to imitate [32]. This ‘new’ science is based on the belief that nature follows the path of least resistance (least expenditure of energy), while often using the most common materials to accomplish a task. Biomimetics, ideally, should be the process of incorporating principles that promote sustainability much like nature does from ‘cradle to grave’, from raw material usage to recyclability, all in this physical world. Biomimetic material chemistry also refers to as bio-inspired chemistry [33] which is an important diverse field such as bio-ceramic, bio-sensing, biomedical engineering, bio-nanotechnology and biologically driven self assembly [5].

Through the history of life on earth, nature has gone through a process of trial and error to refine the living organisms, processes, and materials on planet Earth. The emerging field of biomimetics has given rise to new technologies created from biologically inspired engineering at both the macro scale and nanoscale levels. Biomimetics is not a new idea. Humans have been looking at nature for answers to both complex and simple problems throughout our existence. Nature has solved many of today's engineering problems such as hydrophobicity, wind resistance, self-assembly, and harnessing solar energy through the evolutionary mechanics of selective advantages.

History of Biomemetic Materials

One of the early examples of biomimetic was the study of birds to enable human flight. Although never successful in creating a "flying machine", Leonardo_da_Vinci (1452–1519) was a keen observer of the anatomy and flight of birds, and made numerous notes and sketches on his observations as well as sketches of various "flying machines" [34]. The Wright_Brothers, who succeeded in flying the first heavier-than-air aircraft in 1903, derived inspiration from observations of pigeons in flight [35]. Otto Schmitt, an American academic and inventor, coined the term biomimetics to describe the transfer of ideas from biology to technology. The term biomimetics only entered the Websters Dictionary in 1974 and is defined as "the study of the formation, structure, or function of biologically produced substances and materials (as enzymes or silk) and biological mechanisms and processes (as protein synthesis or photosynthesis) especially for the purpose of synthesizing similar products by artificial mechanisms which mimic natural ones".

In 1960, the term bionics was coined by psychiatrist and engineer Jack Steele to mean "the sciences of systems which have some function copied from nature" [32]. Bionics entered the Webster dictionary in 1960 as "a science concerned with the application of data about the functioning of biological systems to the solution of engineering problems". The term bionic took on a different connotation when Martin Caidin referenced Jack Steele and his work in the novel "Cyborg" which later resulted in the 1974 television series "The Six Million Dollar Man" and its spin-offs. The term bionic then became associated with 'the use of electronically operated artificial body parts' and 'having ordinary human powers increased by or as if by the aid of such devices' [36]. The term bionic took on the implication of supernatural strength, the scientific community in English speaking countries largely abandoned it [37].

The term biomimicry appeared as early as 1982 [38]. The term biomimicry was popularized by scientist and author Janine Benyus in her 1997 book Biomimicry: Innovation Inspired by Nature. Biomimicry is defined in her book as a "new science that studies nature's models and then imitates or takes inspiration from these designs and processes to solve human problems". Benyus suggests looking to Nature as a "Model, Measure, and Mentor" and emphasizes sustainability as an objective of biomimicry [39].

Biological material science is developing rapidly as a new field at the interface between materials science and biology. The reasons are quite are diverse [40]. First, the advance in regenerative medicine generates an ever growing need for new types of biomaterials with specific and well-defined interaction with the biological host system [3, 7]. Secondly, recent advances in material characterization and fabrication technologies have prompted scientists to ask how one can reformulate the structure of natural materials, which developed in the course of evolution, into biomimetic designs for engineering applications [5, 6]. This leads to new classes of advanced materials with unusual combination of properties, which self-assemble, repair themselves or evolve. Finally, it is increasingly recognized that material properties can be critical for the biological function of molecules, tissues and organs. Hence, material science approach also contribute to some areas of biology [41- 42]. These three different directions constitute the vast and growing field of biological material science (the Figure below illustrates this).

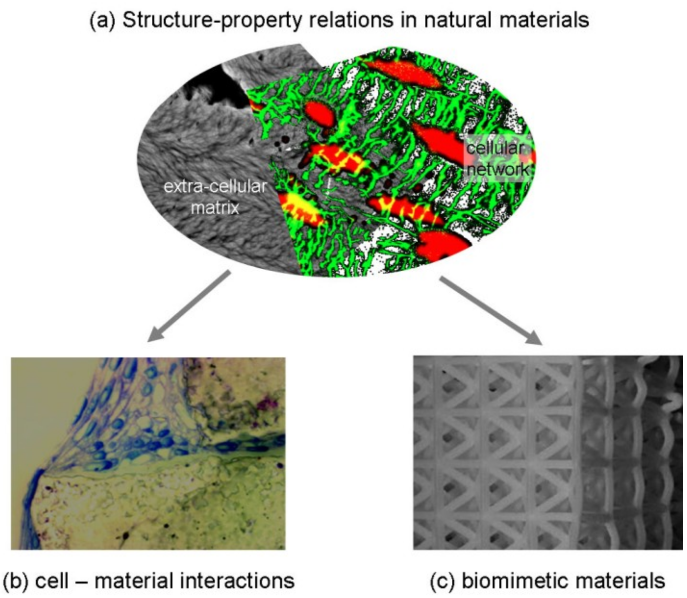


Figure 1: Three research areas of biological material science exemplified by research on bone:

(a) Material science approaches are used to elucidate structure-property relations in biological materials. Light and electron microscopic pictures show the cellular network of osteocytes and the mineralized extra-cellular matrix surrounding them. (b) A better understanding of cell – material interactions will, for example, improve implantable biomaterials and tissue engineering. The image shows bone forming cells growing on a ceramic scaffold. (c) Design principles of natural materials may help in developing new materials with unusual properties. The picture shows a biomimetic scaffold built by rapid prototyping.

Biomimetic Approach in Inorganic Material Chemistry

Biomimetic approaches in material chemistry are at present primarily focused on in the study of processes and properties at the inorganic organic interface [43-44]. These strategies can be embraced within three activities which are (i) nanoscale synthesis, (ii) crystal engineering and (iii) microstructural fabrications – that are related to different combinations of the three biological constructional processes [45].

Nanoscale Synthesis. Due to of the fact that nanoscale particles show quantum size effects in their electronic, optical and chemical properties, there has been much activity in this area of synthetic chemistry [46]. A complementary biomimetic strategy involves the use of organic supramolecular cages that act as spatial hosts and reactive interfaces for inorganic guest materials, reverse micelles [47-48], microemulsions [49-50] and surfactant vesicles [51-52]. They have been used in a number of studies involving semiconductor, catalytic and magnetic materials (Table 1) [45]. These systems often have limited stability with regard to aggregation and hydrolysis, although the use of polymerized vesicles has ameliorated some of these problems. An alternative approach is to use the bimolecular cage of the iron-storage protein ferritin as a more robust environment for inorganic material synthesis [53-54]. In situ chemical reaction of the native iron oxide ores readily produces nanoscale iron sulphides. Whereas, the reconstitution of empty protein cages in aqueous salt solution gives a range of non-native oxide materials. One of which, magnetic Iron oxide, (Fe_3O_4), endows the protein with permanent magnetic properties [54]. Other approaches that are not strictly biomimetic in design (e.g. the intercalation of nanoscale particles of CdS in Langmuir-Blodgett films [55] and magnetic iron oxides in polystyrene resins [56] serve to illustrate the general importance of inorganic-organic interactions in the control of material synthesis.

Crystal Engineering. Controlling the nucleation and growth of inorganic materials is an important consideration in material and colloidal chemistry. Oriented inorganic substrates such as Au and Si are used as epitaxial surfaces in chemical vapour deposition methods, and it would be significant if similar processes could routinely be undertaken in aqueous solutions. Over the past few years, a biomimetic approach to crystal engineering has been developed [45]. For example, compressed Langmuir monolayers have been used as nucleation substrates for the oriented growth of inorganic materials [57-61]. One particular advantage of this approach is that the functionality and packing of the organic surface is readily modified. Indeed, in many instances, complementing between the surface chemistry and structure of the surfactant film, and crystal faces of the incipient nuclei, results in the oriented nucleation of two-dimensional arrays of discrete crystals at the monolayer solution interface [45]. Another approach involving the adsorption of polyasparate onto a sulphonated polystyrene surface [62] was also effective in controlling oriented nucleation. These experiments, like those involving monolayers, highlight the requirements for molecular periodicity because the adsorbed molecules must adopt a β-sheet conformation if oriented nucleation is to be induced.

Biomolecular surface, such as tubules [63-65]. Bacterial fibres [66], rhapidosomes [67], and S-layer proteins [68], have been used as structural templates to guide the deposition of inorganic materials within predetermined spatial patterns [45]. The resulting crystals are often randomly arranged, but the microscopic morphology is controlled. In particular, elongated fibrous inorganic-organic composites can be formed [45]. The crystal morphology and texture of inorganic materials can also be influenced by soluble biomolecules. For example, acidic macromolecules (isolated from sea urchins) influence the morphology and fracture of synthetic calcite crystals by surface recognition and site-specific occlusion, respectively [69-70]. Studies using synthetic-peptide analogues of these biomolecules suggest that polyanionic domains of polyasparate and serine phosphate are responsible for the functional activity of the shell proteins [71].

Microstructural Fabrication. Controlling the microstructure of biominerals by cellular processing is clearly the most difficult aspect to translate into the world of material chemistry. The sophisticated use of cellular activity in shaping and assembling biominerals is difficult to reconcile with the static methods of chemical fabrication. Some progress has been made, however, in the use of functionalized polymers [72-75], polymer gels [76] and biomolecular matrices [77] as organized frameworks for in situ inorganic precipitation [45]. One of the main problems is the low mineral content of the resulting inorganic-organic composites [78]. One possible way round this is to run the system in reverse, that is, to incorporate a soluble polymer (polyethylene oxide into a preformed mineral matrix (such as the interlayers of a mica [79] or alternatively, precipitate both mineral (calcium silicate/aluminate) and polymer (polyvinyl alcohol) simultaneously [80-81]. It will be interesting to determine how the mechanical properties of these organoceramics compare with those observed in biominaerals such as abalone shell [43].

Table 1: Biomimetic approaches in inorganic material chemistry [45].

APPROACH	STRATEGY	PRODUCT	SYSTEM	MATERIALS
Nanoscale synthesis	Host guest	Cluster	Reverse micelles Microemulsion	CdS Pt, Co, Metal Borides Fe_3O_4, $CaCO_3$
		Nanoparticles	Vesicles	Pt, Ag, CdS, ZnS, Ag_2O, FeOOH, Fe_3O_4, Al_2O_3 Ca phosphates
			Ferritin LB film Polystyrene resin	MnOOH, UO_2, FeS, Fe_3O_4 CdS γ-Fe_2O_3
	Ligand capping		$(\gamma\text{-EC})_nG$ peptide	CdS
Crystal engineering	Oriented nucleated	Single crystal	Monolayer PolyAsp/Polystyrene	NaCl,$CaCO_3$,$BaSO_4$,PbS $CaCO_3$
	Templating	Shaped composites	Tubules Bacteria fibres Bacterial rhapidosomes	Cu, Ni, Al_2O_3, Fe oxides Fe_2O_3, $CaCO_3$, CuCl Pd
		Textured crystals	S-layer proteins	Ta/W
	Directed growth		Sea urchin proteins Polyanionic peptides	$CaCO_3$ $CaCO_3$
Microstructural fabrication	Extended frameworks	Mineral-polymer composites	Polystyrene-butadiene Polyvinylchloride Polyacrlate films Polysiloxanes Plyethylene oxide Collagen	$CaCO_3$, CdS, Ca phosphate TiO_2 Fe oxides, $BaTiO_3$ $CaCO_3$, $CaSiO_3$ CdS Ca phosphate
	Assembly	Organized materials	Monolayers /Au Monolayers Cast bilayers films Hydroxyl ethylcellulose Polyacrlate sols SiO_2/OH^-gel	 CdS Fe_2O_3 Fe_3O_4 $CaCO_3$ $BaSO_4$ $CaCO_3$

Biomimetic Material Synthesis

The aim of this approach is to explore the possibility of generating new material families of great potential using ideas from biological systems. Clearly this type of research has to rely on a thorough study of the structure-function relationship of the biological materials which may serve as models. Rather than copying the structures observed in nature, the building principles are being transferred which requires a deep understanding of the biological model system [1]. Within the profile of material science activities of the Max Planck Society, involving Institutes in Potsdam, Mühlheim, Dresden, Stuttgart, to name just a few, a whole variety of approaches has proven successful in transferring working ideas from the study of biological systems into a chemical or technical environment. One of those areas is biomimetic mineralization [40]. Biominerals, such as mother of pearl, are materials usually generated from available commodities or waste products but with superior properties to man-made materials of the same composition. This is due to their composition, structural hierarchy and a clever composite or hybrid design. It was therefore very attractive to unravel the natural design principles and to apply them in biomimetic mineralization approach [40].

Biominerals are usually synthesized at the surface of organic templates such as macromolecular frameworks, lipid membranes or cell walls. In order to achieve these biomineralization processes, specific interactions, selective organic moieties and biocompatible minerals have evolved. A recent study has shown the complexity underlying cell/mineral interactions in the case of the bacterium, *Shewanella oneidensi* and iron oxide minerals, goethite (α-FeO (OH)) [82]. *Shewanella oneidensi* is a dissimilatory metal-reducing bacterium, which oxidizes organic matter in oxygen-deficient environments by reductively dissolving iron (III)-rich minerals.

The general importance of proteins and peptides in controlling the nucleation and/or growth stages of mineralization has continued to be demonstrated by many in-vitro studies of calcium carbonate crystallization. For example, chiral crystals of calcite were formed in the presence of pure D-or L-aspartic acid due to preferential binding of amino acid enantiomers to the surface steps that offer the best geometrical and chemical match [83]. Homo-or heteropolymers of amino acids also have a marked influence on calcium carbonate crystallization [84].

It turned out that biominerals are not formed along the classical crystallization pathway. Instead, mutual organizations of nanoparticle building units as well as amorphous and possibly even liquid precursors seem to be important. Setting the conditions such that these pathways can also be used in technical crystallization processes has lead to the generation of complex synthetic crystalline structures, which are indeed organic-inorganic hybrid materials, often exhibiting hierarchy. Mimicking nacre as a layered hybrid structure has been pursued within the Max Planck Society (MPS) [85-89], and elsewhere [90-91]. Indeed, nacre is a layered composite of calcium carbonate mineral and macromolecules with 3000-fold fracture resistance compared to the mineral itself. Using synthetically generated liquid precursors for the mineral phase to infiltrate the organic scaffold of Nacre which allows generating a material that cannot be visually distinguished in its structure from natural Nacre – even not under an electron microscope [85]. Other work in Dresden focuses on biomimetic morphogenesis and structures of hierarchical nanocomposite superstructures closely related to functional materials in the human body (bone/teeth and otoconia) [92-93] because these biominerals are very rich in calcium which are useful in the formation of strong bone and teeth.

The influence of polyacrylic acid on $CaCO_3$ crystallization has been reported by Naka and Chujo [84]. They showed that the precipitation of one of the three polymorphs of $CaCO_3$ can be induced at low temperature (30^0C) by triggering the polymerization of acrylic acid after different aging times in a calcium carbonate supersaturated solution. The cooperative effect of aqueous solutions of poly (acrylic acid) and insoluble polysaccharide substrate (cellulose, chitin, chitosan) has also been studied. When all proton-donor or – acceptor groups of the polysaccharides are protected, no precipitation occurs. In the presence of NH_2 and/or OH groups on the solid surface, but without the polymer solution. A variety of synthetic substrates and their effect on the controlled morphogenesis of calcium carbonate have been reviewed recently [84].

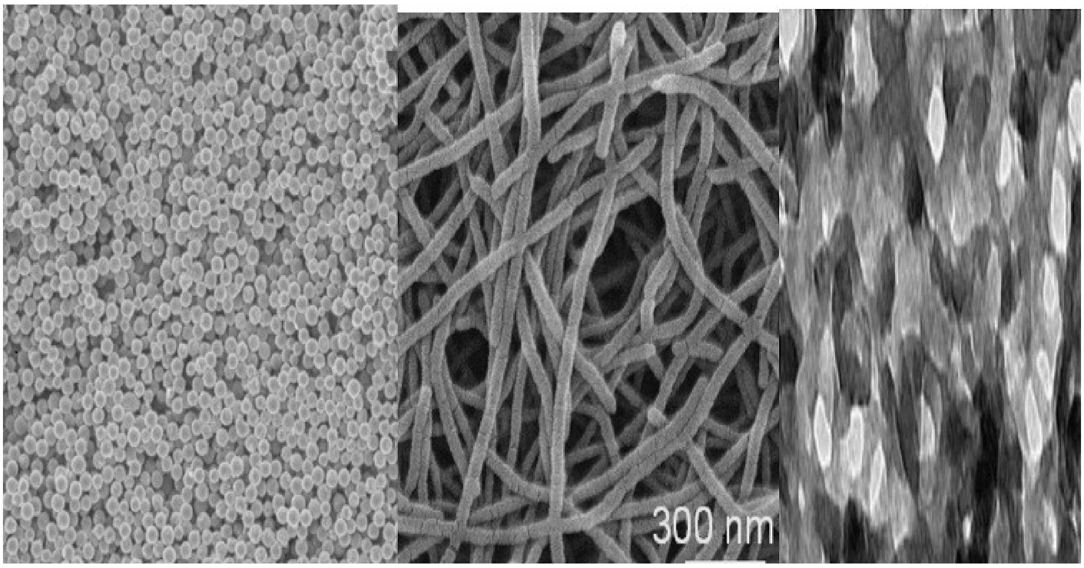
Compared with calcium carbonate, fewer studies were reported in 2001 on the effect of organic macromolecules on calcium phosphate crystallization. One remarkable system, however, concerned the study of fluoapatite – gelatin composites as a model system for building nano – and meso-structured materials exhibiting some of the characteristics of tooth enamel [94]. As chemistry is not bound to $CaCO_3$ but can employ better performing technical solutions, such biomimetic approaches are highly promising for future material design, as they can be extended by using carbon fibers, alumina flakes, or WC- nanostructures [40]. Ongoing work at the MPI Stuttgart focuses on the generation as well as the investigation of the structure-property relationships of inorganic functional materials and organic/inorganic hybrids, based proteins, peptides, amino acids, and DNA as well as synthetic polyelectrolytes or self-assembled monolayers serving as organic templates for the formation of oxide-based materials with superior mechanical properties [87-88]. Further research efforts deal with surface display methods in order to identify peptides, which specifically interact with inorganic functional materials and thus guide the formation of organic/inorganic composite materials. Besides this combinatorial biological approach to discover mineralizing peptides, the identification of bacterial proteins, directing mineralization in microbes is currently studied [40]. Furthermore, the investigation also comprises of unicellular microalgae, which makes use of polysaccharides as templates for biomineralization.

Porous structures offer a large heterogeneous surface for exchange reactions, e.g., for chemical reactivity (in heterogenous catalysis for electron exchange in electrodes) or for molecular adsorption (for adsorbents and chromatographic materials). However, most technical systems exhibit either a regular porosity (e.g. zeolites) or even a random porosity, such as activated carbons. This is not favourable and results in serious technical restrictions of mass transport and mass exchange. Nature, on the opposite, has found a different solution for this problem and establishes a hierarchical transport and pore system to combine optimal surface area with minimal resistance [40].

Biomimetic science not only contains the inspiration by natural materials but also natural processes, partly. Hydrothermal processes or the formation of coal or fossil fuels from biomass are just good examples to illustrate this type of processing and thinking. Mimicking coal formation from biomass in the laboratory opens special perspectives, as waste biomass is omnipresent on this planet; while coal or carbon derived materials are regarded as high value product in this world of ours. Biomimetic approaches to diverse long lasting carbon structures by optimization and variation of synthetic procedures include "biomimetic humins" [40] or black porous carbon as a conditioner to improve soil quality (thus generating "black soil" from depleted soil), ion exchange carbons for ion binding or with improved sorption capacity to clean drinking water since adsorption onto activated carbon in the form of grains or powder is a well-known process for micropollutants removal. In recent years, new adsorbents have been developed: cloths made of woven activated carbon fibres. These activated carbon cloths exhibit a low diameter of fibres (10μ m), a large microporosity volume as well as high specific surface area which may reach 2,000 m^2 /g [95]. With such characteristics, these adsorbents are shown to be efficient in adsorbing micro organic pollutants from aqueous or gaseous streams [96], but also high carbon hybrid materials which can effectively be used in the future generation of lithium batteries, similar to the approach described above but on the basis of biomass.

It is therefore interesting to note that changing the raw material base to carbon-negative sustainable biomass does not necessarily compromise the carbon properties, for instance, literature-described battery capacities well above the current technology level, and the ion exchange capacity of the synthetic humin ion exchangers is by factors higher than the best commercial, petrochemical ion exchange resins [40].

Other research topics that are currently treated include CO_2-specific sorbents for carbon capture and storage schemes or – giving up CO_2 negativity- the development of an indirect carbon fuel cell which turns aqueous dispersions of hydrothermal coal directly into electric energy [40]. Thus, using the colloids derived from hydrothermally treated biomass (including banana and orange peels), such fuel cells have shown to be operative and can act as a potential source of electricity with an overall zero-emission balance of CO_2 . especially the black humin carbon used for soil improvement seems to have the potential for taking up a significant part of CO_2 from the atmosphere while generating a biological benefit at the same time, via higher crop yields of farmland or a potential reforestation of badlands [40]. The biomimetic process (from an expert's view) can provide an effective and sustainable alternative to the currently known "biochar" process (using dry biomass and classical charring) [40]. The figure below depicts some of the possible carbon structures made by high-temperature catalysis to illustrate that biomimetic chemical processes can extend nature to a range where bio-geological processes are simply not operative.



(a) (b) (c)

Figure 2: Different carbon nanostructures made by high-temperature catalysis, mimicking natural coalification however in a controlled technological environment: a) carbon nanoparticles for printing or reinforcement; b) carbon nanorods as texture modifier or conductance additive; c) sponge like carbon for water binding and ion exchange

Among many other interesting options of so called "molecular fossils" (i.e. molecules existing in nature throughout evolution), organic semiconductors based on CO_2, ammonia and/or prussic acid are chemically appealing. It is interesting that following those ideas (and Justus Liebig´s pathways) it was recently possible to synthesize an all organic polymeric semiconductors from urea (or CO_2 and ammonia) which is extremely oxidation stable and therefore exhibits the appropriate band gap to split water photochemically and to activate CO_2 [97]. The efficiencies are still rather low, but the principal feasibility includes the rather robust generation of organic indirect semiconductors which was rather unexpected i.e a posteriori which justifies the primary assumptions of a near bio-geo-mimetic approach.

Cell Material Interaction and Mineralized Biology

One of the many remarkable features of bone is the integration of living cells within the mineralized collagen matrix. Not only are the cells biochemically active but they also communicate to other as well as cells outside the tissue so that the mineral becomes an integrated system capable of adaptation. The synthesis and processing of analogous artificial systems is far from being realized and represents a major challenge and paradigm shift in biomimetic material chemistry.

Currently, there are many studies describing the encapsulation of biomolecules within inert inorganic matrices such as silica. In many cases, the biomolecules are used as functional units within a porous medium. For example, chlorophyll *a* and *b* pigments have been chemically grafted post-synthetically unto the internal surfaces of a mesoporous silica modified with α, *w*-diols [98]. In contrast to studies on molecular entrapment, there are few investigations on the incarceration within inorganic matrices of proteins or whole cells; however, the field appears to be developing. One of the major issues is to immobilize these relatively large biological components in the solid matrix without loss of structural integrity and functionality, and in this regard, the soft conditions of sol-gel processes appear to be very promising. Other studies have cast intact biostructures in silica. For example, highly ordered silica replicas were produced by surfactant-assisted mineralization of wood tissues [99].

The way biomaterials interact with a biological system raises a number of fundamental unresolved questions [40]. Cells have been shown to respond not only to subtle variations in the chemical composition of the growth medium and to contacts with neighbouring cells, but also to the nature and the properties of the materials they are in contact with. This concern on how cell interact with materials, can influence cell growth and differentiation by the properties of a substrate material. This includes physical properties, such as stiffness, shape, roughness, porosity of the surface, as well as chemicals, such as the role of surface functionalization or protein adsorption. Resolving such questions is crucial in the context of regenerative medicine, in biomedical engineering or even in the control of biofouling. A number of Institutes of the MPS, including those in Göttingen, Munich, Stuttgart, are engaged in such studies. For example, work at the MPI of metal research has shown that the spacing of possible binding sites on a material surface in the nanometer range has a profound influence on the adherence of cells and, thus, on their capacity to proliferate next to the material [40-41, 101-102].

One of the most stricking characteristics associated with many biominerals is their exquisite ornamentation. The subtle and intricate decoration of diatom frustles, coccolith scales and acantharian skeleton arises from the dynamic shaping of vesicles under cellular stresses. Simple elongated morphologies are probably produced by affiliation of the vesicles with cytoskeletal frameworks such as radial (tubulins) or tangential (spectrins) stress filament [45].

Biologically Inspired Engineering

The use of biomineralized structures is vast; they are derived from the abundance of nature through studying the nano-scale morphology of living organisms, many applications have been developed through multidisciplinary collaboration between biologists, chemists, bioengineers, nanotechnologists, and material scientists. For example, the biomimetic materials in tissue engineering are materials that have been designed such that they elicit specified cellular responses mediated by interactions with scaffold-tethered peptides from extracellular matrix (ECM) proteins; essentially, the incorporation of cell-binding peptides into biomaterials via chemical or physical modification [103]. Such peptides include both native long chains of ECM proteins as well as short peptide sequences derived from intact ECM proteins. The idea is that the biomimetic material will mimic some of the roles that an extracellular matrix plays in neural tissue.

Diverse Use of Fibres

Nature is full of excellent examples of building with fibres. A more obvious example is in the cobwebs formed by certain species of spiders. These are made up of short irregular strands of fibres arranged almost randomly while the cob-webs made by other species of spiders are regular, elegant and elaborate. Plants and trees provide other superb examples of fibrous structures. In many cases, the fibres are arranged or oriented in a particular manner to impart desired mechanical properties to the structure. A good example is the coconut palm (*Cocos nucifera*, Linn.) tree [104]. The coir fibre derived from its seed husk is well-known and used in floor coverings, mattress fillings and others. Among other fibres found on a coconut palm [105], the layers of fibrous sheets in the leaf-sheath (base of the leaf stalk attached to the tree trunk) with fibres in the alternating sheets oriented nearly orthogonal to each other appear to be already in a woven structure [106]. Interestingly, the leaf-sheath consists of three distinct types of multicellular fibres made of mostly cellulose and lignin arranged in a highly ordered structure. The mechanical properties of these three types of leaf-sheath fibres are different from each other [106]. Wood and bamboo are excellent examples of natural fibrous composites with high work of fracture. Wood consists of parallel hollow tubular cells reinforced by spirally wound cellulosic fibrils embedded in a hemicelllulose and lignin matrix. The helix angle of the spiral fibrils control various mechanical properties including stiffness and toughness of wood [107-110]. Bamboo is one of the strongest natural fibrous composites with many distinguishing features. It is a hollow cylinder with almost equidistant nodes. Bamboo also has a functionally graded structure in which fibre distribution in the cross section in the bamboo's culm is relatively dense in the outer region [111]. The chemical composition of bamboo is very similar to wood but its mechanical properties are very different. Wood tracheid and bamboo fibres [112-113] are both hollow tubes (or with a lumen) composed of several concentric layers, each layer is reinforced with helically wound microfibrils. The difference in properties originates from the number of fibre layers and microfibrillar orientation angles [112].

Nature also has abundance of examples of responsive fibrous structures. Many plants are able to produce passive actuation of organs by controlling anisotropic deformation of cells upon exposure to moisture.

Plant cell walls are made of stiff cellulosic fibrils embedded in a moisture-sensitive softer matrix consisting of hemicelluloses, pectin and hydrophobic lignin. The absorption and desorption of moisture by the plant cell wall matrix causes anisotropic deformation of the cell wall [114]. The orientation of the cellulosic fibrils in the cell walls as well as their stiffness is crucial in determining the degree as well as the direction of the bending actuation [115]. Pine cones are known to use this hygromorphic behaviour in distributing their seeds. Drying at ambient humidity causes a close and tightly packed pine cone to open up slowly owing to the bilayered structure of the individual scales [115-116]. The mechanism of pine cone opening relies on the humidity sensitive outer layer of the ovuliferous scales to expand or shrink in response to moisture in the atmosphere, while the inner layer remains relatively unresponsive [115].

From plants to animals, one of the unique uses of fibres in structural construction is that of the skeleton of glass sponge *Euplectella* as reported by Aizenberg [117]. The hierarchical structure is made of lamellar fibres of silica nanospheres at the nanoscale to rectangular lattice formed by rigid fibre-composite beams at the macroscale. The resulting remarkable truss-like cylindrical, skeletal structure made of the intrinsically low strength and brittle material, glass, is stable and is able to withstand tensile and shear stresses caused by currents while attached to the ocean floor. Interestingly, the structure is very similar to that of a triaxial fabric developed by Dow in 1969 to obtain a more 'isotropic' and stable structure appropriate for space applications [118].

Biomimicry and Sustainability

Biomimicry, in its strictest interpretation, is the process of emulating nature's way of finding a solution including 'designing' and 'making' with the least environmental impact. In fact, biological systems should be seen more as concept generators in terms of transfer of principles and mechanisms rather than something to copy, literally. Modern technologies have made it possible to design and manufacture products/systems that are based on nature. However, the process or the technology to do so has not always been purely eco-friendly. It is primarily because nature's implementation of a concept into a system is far different than that developed by humans. In nature, growth is the primary means of 'manufacture' rather than fabrication. The hook and loop fastener, Velcro, has been traditionally manufactured using nylon. The key ingredients are petroleum derivatives, with the usual environmental consequences of petroleum processing. If biomimicry is to be used as a new principle in designing fibres(e.g. textiles), sustainability must be part of it. Biomimetics can help us rethink our approach to material development and processing thereby help to reduce our ecological footprint [104]. The history of textiles is full of continuous search for invention of new fibre-forming polymers with unique and improved properties. The increase in world population coupled with increased standards of living has driven *per capita* consumption of fibre to levels that may not be sustainable. As an example, *per capita* consumption of fibres in the USA has grown from about 25 kg in the early 1980s to about 40 kg in 2008 [119-121]. The increasing demand for fibres is also driven by their new and innovative use in new and innovative products. Ideally, the increasing demand should be met largely by using renewable resources and through efficient recycling. Plants and animals in nature hold the key to this route.

Economic Impact of Biomimetic Materials

The design strategies of biological materials are not immediately applicable to the design of new engineering materials, since there are some remarkable differences between the strategies common in engineering and those used by nature. The first major difference is in the range of choice of elements, which is far greater for the engineer. Elements such as iron, chromium and nickel are very rare in biological tissues and certainly not used in metallic form, as would be the case for steel. Iron is found in red blood cells, for instance, as an ion bound to the protein haemoglobin and its function is certainly not mechanical but rather to bind oxygen. Most of the structural materials used by nature are polymers or composites of polymers and ceramic particles. Such materials would generally not be the first choice of an engineer to build strong and long-lasting mechanical structures. Nevertheless, nature uses them to build trees and skeletons. The second major difference is the way in which materials are made. While the engineer selects a material to fabricate a part according to an exact design, nature goes the opposite way and grows both the material and the whole organism (a plant or an animal) using the principles of (biologically controlled) self-assembly. This provides control over the structure of the material at all levels of hierarchy and is certainly a key to the successful use of polymers and composites as structural materials.

Bio-inspiration is not just a consequence of an observation of naturally occurring structures [122]. The reason is that nature has a multitude of boundary conditions which we do not know apriori and which might all be important for the development of the structure observed. Therefore, we need to keep our eyes open and must be able to solve a particular problem set. Both the biological structure and the set of problems the structure is designed to solve can bio-inspire us. For example, the structure of our own femoral head to be a solution for a mechanical optimization problem (as hypothesized in the so-called Wolff law) [123] is a practical example, questions still remain like which mechanical property has been optimized (stiffness, toughness and defect tolerance) and the possible influence of other boundary conditions. It is well known that bone is also the body's ion reservoir and serves the calcium homeostasis [124] it is phrased in the question, 'If bone is the answer, what is the question?' It is quite true that the structures we observe are probably good solutions found by a long adaptation process during evolution.

III. Other important impact includes

1. **Damage repair and healing:** One of the most remarkable properties of biological materials is their capacity of self-repair and there are different strategies associated with self-repair. At the smallest scale, there is the concept of sacrificial bonds between molecules that break and reform dynamically [125]. Bond breaking and reforming was found, for example, to occur upon deformation of wood and bone [126-130]. This provides, in fact, the possibility for plastic deformation (without creating permanent damage) as in many metals and alloys. At higher levels, many organisms have the capability to remodel the material. In bone, for example, specialized cells (osteoclasts) are permanently removed material, while other cells (osteoblasts) are depositing new tissues.
2. **Growth and functional adaptation**: This can be influenced by the external conditions such as temperature, mechanical loading, and supply of light, water or nutrition. The living organism must necessarily possess the ability of adaptation to external needs, while possible external influences on a technical system must be typically anticipated in its design, leading to considerable 'over-design' [104]. This aspect of functional adaptation is particularly fascinating for the material scientists, since several undiscovered solutions of nature can serve as sources of inspiration [131]
3. **Hierarchical structuring**: This is one of the results of the growth process of organs. Examples of such hierarchical biological materials are bone [131-134], trees [126, 135-136], superhydrophobic surfaces (Lotus effect; [137-139]. Clearly, hierarchical structuring provides a major opportunity for bio-inspired material synthesis and adaptation of properties for specific functions [140]. Hierarchical hybrid materials can also provide movement and motility. Muscles and connective tissues are integrated to form a complex materials system which is both a motor and supporting structure at the same time. This may inspire material scientists to invent new concepts for active biomimetic materials [141-147].

Challenges and future prospect

The remarkable ability of biological organism to recognize, sort and process diverse and complex sources of information continues to inspire novel approach and in- depth knowledge with respect to the fabrication of inorganic-based surfaces and interfaces. The complex functions that have naturally evolved in the biological world therefore needed to be used routinely in the future to confer advanced capabilities to the man-made materials and architectures.

It is now very important to adopt a loose definition for the term biomimetic material chemistry; the reason is because there are lots of conceptual overlap between those approaches that are inspired by biology and those ones that are based on molecular engineering in material chemistry. The major challenge here is how to translate the harsher regimes of current fabrication technology into the mild that is low temperature and pressure chemical conditions characteristic of biomineralisation.

Unfortunately, we do not know exactly which problem has been solved. It may be to provide a strong material and also to meet some different biological constraints. This implies that we may not succeed if we follow without modifications the solutions found by nature as optimal for a certain unknown requirement. So, we have to carefully study the biological system and understand the structure–function relationship of the biological material in the context of its physical and biological constraints. Careful investigation of a biological system serving as the model is necessary for biomimetic material research.

Another important challenge is that biomineralization is associated with absence of toxic intermediates and therefore one will certainly do well to incorporate this biological rule of construction in assessing the impact of future material fabrication process on our environment.

There is also a need to ask question on how inorganic materials can be assembled by molecular structure of the earth crust (tectonic) into the organized long-range architecture. It is now ripe to have a biological view of inorganic material chemistry, the concepts: such as self-organization, replication, synergism, morphogenesis, transcription, and metamorphosis. These will be useful in constructive thinking about novel way of synthesizing inorganic materials that exhibit a complex form across the range of lengthy scales. This however suggests a desperate field that can conceptually linked biological assembly and inorganic material chemistry such as biomineralization and biomimetic material chemistry. This in fact, is a serious challenge.

Lastly, this new insight is required to be developed as to the preparation of biocompatible materials and interfaces which will accelerate the creation of probes, sensors and implants for use in the bionic system of matter; this will depend on advances in our knowledge of native biological materials, such as biominerals.

IV. Conclusion

There is ample evidence to suggest that our ancestors looked to nature for inspiration to conceive new materials and devices long before the term biomimetic was coined. It is unclear what inspired prehistoric humans to invent the processes (i.e. spinning, weaving, etc.) to assemble fibres into clothing; it may have been an orthogonally interlaced thin and flexible biological structure like the coconut leaf sheath, or the nest of a weaver bird, or it may have been an invention of a contemporary genius. The fundamental practice of prehistoric humans to produce textiles from natural fibres has evolved into a vast array of modern energy- and resource-intensive technologies to make high-performance fibres and manipulate these fibres into complex textile structures for applications in civil construction, filtration, healthcare, etc., in addition to clothing.

Nature provides us with a plethora of techniques to build with fibres to achieve specific goals, and there is tremendous potential to learn from it. Understanding the structure–function relationships is the key in developing textile products that are, for example, adaptive, thermo-resistant, superhydrophobic, or self-healing, examples of which are plentiful in nature. The obvious need for sustainability requires not just mimicking natural design but also the process. A few of these have been covered in this review. The field remains wide open for continuous scientific exploration. The concept of hierarchical structuring for the development of multi-functional materials through optimization at various scales is relevant for many of today's textile structures and applications. Transfer of a concept from natural to man-made is not trivial. However, as Vincent noted 'there is a huge potential to obtain new or unusual combinations of material functions/properties by structuring a given material, rather than by changing its chemical composition'. In fact, textile fibre assemblies can readily provide an ideal test-bed for this concept.

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