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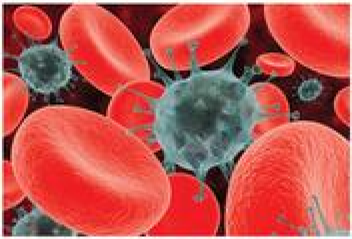

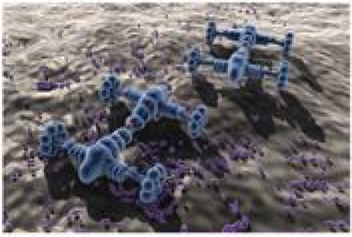

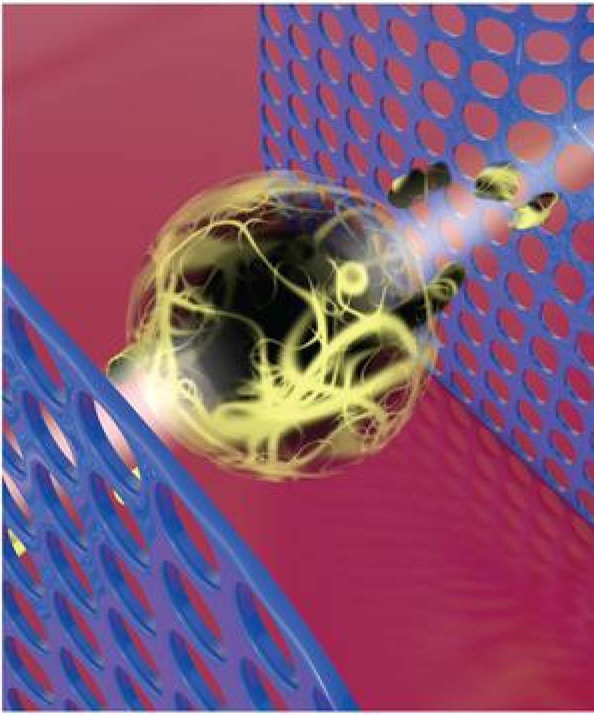

Edited by
Boris Ildusovich Kharisov • Oxana Vasilievna Kharissova • Ubaldo Ortiz-Mendez

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To my grandfather Arsenii P. Chekalov and my grandmother Anna A. Chekalova

Boris Ildusovich Kharisov

To my mother Olga V. Chubur

Oxana Vasilievna Kharissova

To my wife, my daughters, and my son

Ubaldo Ortiz-Méndez

Contents

Preface

This encyclopedia has been written by leading professionals in the field worldwide. The chapters are arranged alphabetically to simplify its use by readers. We expect that our book will be useful not only for specialists (professors, researchers, engineers), but also for undergraduate and graduate students. On the whole, the target audiences are as follows: students, scientists, college and university professors, research professionals, technology investors and developers, research enterprises, R&D and defense research laboratories, and academic and research libraries. These very broad spectra of specialists work in the fields of nanotechnology and nanoscience and have strong connections with materials science, electrical and electronic engineering, solid-state physics, surface science, catalysis, "greener" chemical processes, colloid science, ceramic and chemical engineering, coatings and adsorbents, drug delivery, polymer science and engineering, sol-gel science, supramolecular science, nanomedicine, metallurgy and powder technology, device and chip engineering, aerospace engineering, computer technology, information technology, environmental engineering, biomimetics, pharmacy, biotechnology, water splitting and remediation, etc.

Students can easily find any data on classic nanotechnology in this book and use them in classroom presentations. Professionals can use the book as a background for their research work, presentation in congresses, and lectures for graduate and postgraduate students in most universities worldwide. The book contains a host of illustrative material in black and white, and the accompanying e-book contains all of the figures/images in full color. You can access the e-book using the code provided on the inside cover of this book.

Placing specialists at the forefront of the nanoscience revolution, this book identifies current challenges and development paths sure to influence fields examining the design, application, and utilization of devices, techniques, and technologies critical to research at the atomic, molecular, and macromolecular levels ranging from 1 to 100 nm. We hope that this encyclopedia will be an invaluable reference source for the libraries of universities and industrial institutions, of government and independent institutes, and for individual research groups and scientists working in the fields of nanoscience and nanotechnology.

The editors are very grateful to the contributors for their hard work and patience.

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Biomimetics: Biomimetics in Nanotechnology

Ille C. Gebeshuber and Manfred Drack

CONTENTS

INTRODUCTION

This chapter deals with the biomimetic method in nanoscience and nanotechnology. Predictability on the basis of scientific understanding is a precondition for technology. The aims of science are to *explain* and *understand* and to *organize knowledge*. With a solid scientific basis, it shall be possible to *make predictions*, for example, about the movement of planets or asteroids, molecules, water flow around pillars, or emergent properties such as bird flock flying patterns and swarm intelligence in ants. To achieve this, various techniques and methods are applied.

Nanoscience and nanotechnology tools and techniques have rapidly developed since the 1980s. Current tools and techniques for characterization, manipulation, and fabrication of matter at the nanoscale are manifold. The four major groups of nanoscale probing tools are scanning probe microscopy, (including scanning tunneling microscopy, atomic force microscopy (AFM), and scanning near field optical microscopy), as well as electron microscopy, x-ray methods, and optical techniques (Bhushan 2010). The core tool, the AFM, was invented in 1986 (Binnig et al. 1986). This lenseless microscope has subnanometer resolution, can be used for imaging as well as *manipulation* down to the single atom level, and works in various environments such as vacuum, air, water, buffer solutions, and oil (Haugstad 2012). This makes it so interesting for applications regarding the investigation of biological samples (Parot et al. 2007). Even live cells (Henderson 1994) or protein–protein interactions on the single protein level can be imaged with this device in real time at unprecedented resolution (Viani et al. 2000).

Nanotechnological *products and processes* can be developed on the grounds of nanofabrication (lab scale), molecular manufacturing (manufacture of complex nanoscale structures by means of nonbiological mechanosynthesis and subsequent assembly), and nanomanufacturing (industrial scale) (Bhushan 2010). In such products and processes, nanotechnology can be embedded in numerous aspects of the manufacturing processes. While the physics itself is the same across all length scales, materials and structures have unique size-dependent properties (that may be very different from the properties of bulk material). Also, the smaller the size, the more relevant the structure of the material becomes. Single atoms, molecules and nanostructures exhibit unusual physical, chemical, and biological properties when compared to the bulk material. Gold, for example, has golden coloration at the macroscale and is known as a highly inert material; nanogold colloids, however, exhibit different colors at different sizes and concentrations, and they are not bio-inert (Brown et al. 2008).

The ideas for new nanotechnological products and processes are often rooted in physics or inorganic chemistry. There is, however, also a considerable and expanding body of knowledge at the nanoscale in biology. Such knowledge about materials, structures and functions in living nature can be applied in different ways. One possibility is to use macromolecules or organisms directly, like in biotechnology. Another way is to strive for the understanding of principles behind particular phenomena and to apply them in distinct areas, like in biomimetics. The following focuses on biomimetics.

What we describe here is perhaps a small but probably significant method for nanotechnology, because the role models that can be found in living nature have been tested in evolution since billions of years.

COMMON GROUND OF BIOMIMETICS AND NANOTECHNOLOGY

Most often biology and engineering do not touch on each other (Figure 30). There is, however, an intersection of both fields. Different disciplines are found in this intersection, such as the two distinct fields of biotechnology and biomimetics. Biotechnology is not our concern here; we only deal with biomimetics. The intersection itself can be sliced into pieces according to their scale. By doing so, the field discussed in this chapter can be illustrated like in Figure 30.

In the following, the fields of biomimetics and nanotechnology are characterized in order to investigate how the former can contribute to the latter.

What Is Biomimetics?

Biomimetics is about transferring principles from biology to engineering to enhance and bring up new products and processes for human needs. Although the name and the scientific field were only established in the last decades, the method is an old one. Leonardo da Vinci and his studies of bird flight, for example, eventually have led to airplanes. At the end of the twentieth century, the field of biomimetics became established both methodically and institutionally, leading to an ever-increasing number of applications.

In this recent definition, the main aspects are covered: "Biomimetics combines the disciplines of biology and technology with the goal of solving technical problems through the abstraction, transfer, and application of knowledge gained from biological models" (VDI 6220 2012).

At the core, biomimetics is about understanding functional or operational principles that are at work in biology and results in the abstractions of them in order to find out if they might also work in engineering. This procedure is different from biotechnology, which is not necessarily about transferring principles.

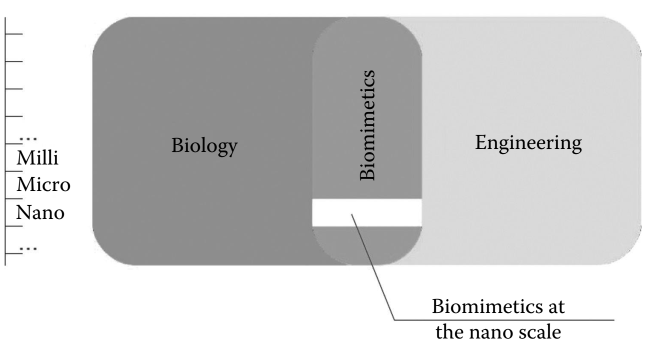

FIGURE 30 Biomimetics and biotechnology are some of the few areas at the intersection of engineering and biology. Biomimetics at the nanoscale is a small but probably significant method in nanotechnology.

Biomimetics works because biological and engineering entities are part of the same world and therefore underlie the same natural laws. Hence, principles in living organisms can also work in technical applications. Nevertheless, there are large differences between entities from the respective fields. One difference is the development throughout which a fertilized egg turns into an embryo and eventually into a mature organism. This is completely different from production devices or machines in engineering. Another difference is that every machine has its engineer who builds it, whereas organisms do not. But this paradigm is slowly changing, with the development of engineered self-replicating machines (see, e.g., Griffith et al. 2005).

Basically, two ways of working in biomimetics can be distinguished. They are referred to as technology pull (also called top-down biomimetics and biomimetics by analogy) and biology push (also called bottom-up biomimetics and biomimetics by induction) (see, e.g., Gebeshuber and Drack 2008).

Technology pull biomimetics is problem based: it starts with a problem in engineering. The next step is to see if similar "problems" occur in living nature. Drag reduction, for instance, is a problem for ship builders and similarly for fish. After such equal problems are found, the biological role models are investigated with the tools and methods of engineering. The term "technical biology" (*Technische Biologie*) was introduced by Nachtigall to name this methodical part of biomimetics (cf. Nachtigall 1998). In the drag reduction case, for example, the engineer would measure relevant parameters of the fish and look at the surface, shape, and so on. In doing so, the researcher might find interesting features, so far not thought about in engineering. The process of finding out more about the principles starts with the potential result of an abstraction that can be transferred and applied in human-built devices or machines.

Biology push biomimetics starts with basic research in biology, without having an application in mind. During or after such work, it might turn out that the found results are also useful for engineering (solution-based biomimetics). The found principles are then transferred and applied.

Technology pull, in general, has a large potential for finding within a short time principles that are useful for particular problems. Utilization of such principles is usually restricted to a small area of application. In contrast, biology push biomimetics has a lower potential for immediate applications, but the chance for finding revolutionary or generic principles is much higher.

Whether a product or technology is the result of biomimetics or not follows from the description of the method. Three necessary conditions have to be fulfilled (i.e., answered with yes) to legitimately speak about biomimetics (Frey et al. 2011, VDI 6220 2012):

1. *Role model from biology*: Did the inspiration come from living nature (biology)?
2. *Abstraction from biological role model*: Was there an abstraction (of a principle) of the natural role

model? Was the biological knowledge analyzed and abstracted step by step (with an understanding of the principle)?

3. *Transfer to technical application*: Was the principle applied in engineering?

The scope of biomimetics is broad. Most of the established knowledge transfer was done in the field of constructions. However, processes in living nature are also of interest, for example, photosynthesis. Furthermore, information processing like in neuronal networks or optimization with genetic algorithms can be referred to as biomimetics (Gruber et al. 2011).

As we have seen, research in biomimetics can lead to applications in engineering. Additionally, the process of doing biomimetics can also reveal new insights for biology, besides those accomplished with technical biology. This can be termed as reverse biomimetics (cf. Masselter et al. 2012, p. 380). One example is the evolutionary strategy of Rechenberg (1994). He introduced algorithms for optimization in engineering based on the concepts of mutation, selection, and recombination from evolutionary biology and achieved good results in engineering. Analyzing those algorithms in turn was of interest for evolutionary biology (cf. Wagner and Altenberg 1996).

What Is Nanotechnology?

According to ISO definition ISO/TS 80004-1:2010, nanotechnology is the "application of scientific knowledge to manipulate and control matter in the nanoscale […] in order to make use of size- and structure-dependent properties and phenomena, as distinct from those associated with individual atoms or molecules or with bulk materials." In a note to this entry, ISO states that manipulation and control includes material synthesis. Nanotechnology has functional parts in the range of nanometers to some hundreds of nanometers. The rise of nanotechnology began when we were able not just to image but also to manipulate matter on the nanometer scale. These possibilities were greatly enhanced with the increasing availability of scanning probe microscopes for the scientific community (Meyer et al. 2004/2012). One of the early examples of nanotechnological manipulation is the spelling of the company name IBM by Don Eigler and coworkers from IBM Almaden with just 35 xenon atoms on a single-crystal nickel surface (Eigler and Schweizer 1990). The group thereby demonstrated tailored manipulation of single atoms.

The two major approaches for obtaining nanotechnological products and processes are termed *top down* and *bottom up* (not to be confused with the terms as used in biomimetics).

> In top-down approaches, nanoobjects are constructed from larger entities without atomic-level control. Top-down approaches comprise lithography, deposition, and etching. In bottom-up approaches, materials and devices are built from molecular components that assemble themselves chemically by principles of molecular recognition. Bottom-up methods include (self-)assembly of atomic and molecular building blocks to form nanostructures. This method is widely used in sol-gel and chemical vapor deposition. In nature, self-assembly has existed for billions of years, from simple biomolecules to complete organisms.
>
> **Gebeshuber et al. (2010)**

The history of nanomaterials can be dated back to pre-Columbian times: The first permanent organic blue pigment, Maya Blue, is a result of ancient "nanotechnology" (Chiari et al. 2008). Further examples of historical nanomaterials are the Lycurgus Cup in the British Museum, dating back to the late Roman Empire, and stained glasses in Medieval Europe (Francis 2010). Properties of nanomaterials are responsible for the respective effects described in this paragraph. It remains to be discussed if it is justified to call such ancient approaches "nanotechnology," since the people back then did not know the reason for the respective material properties.

In general, nanoscience deals with research on materials, structures, and processes on the nanometer scale, and nanotechnology deals with the development of materials, structures, and processes where the functional units are in the nanometer range (generally from a few nanometers to some hundreds of nanometers). Nanoscience and nanotechnology can rather be associated with tools, techniques, and methods than with established research fields. Most research in these fields is rather interdisciplinary and touches upon pure and applied mathematics, physics, chemistry, materials science, engineering, and life sciences. The methods, concepts, and goals of the respective fields converge. This inherent interdisciplinarity of nanotechnology poses a challenge and offers an enormous potential for fruitful cross-fertilization among specialist areas. The properties of many materials change when they exist as nanosized particles. Besides the chemistry, surface physics becomes increasingly important, and not just the material itself but also its structure is of relevance for its mechanical, electrical, catalytic, optical, and toxic properties. Furthermore, quantum effects such as the tunneling effect, confinement properties, spin effects, and quantum coherence are important.

The scope of nanotechnology is to individually address, control, and modify structures, materials, and devices with nanometer precision and to synthesize such structures into systems of micro- and macroscopic dimensions such as microelectromechanical systems-based devices. For this, we need to establisha thorough understanding of the fundamental physics, chemistry, biology, toxicology and technology of nanoscale objects (nanomaterials, nanoparticles, nanostructures), the respective fabrication, diagnostics and analytics and of how such objects can be used in areas such as computation, cosmetics, engineering, medicine, nanobiotechnology, nanostructured materials, optics, resource sustainability, science, sensors, textiles, and many more.

FIELDS OF COMMON POTENTIAL

Phenomena of life occur on different hierarchical levels, down to the nanoscale. The micro- and nanoscale are of specific importance in living systems. Single molecules, their interactions, and emergent properties on larger length scales are the very constituents of life. The complexity of a single cell in the human body by far exceeds any current engineered device. A cell's activities such as sensing, actuation, energy conversion, or information storage are carried out with the contribution of biomolecules, such as proteins. Protein sizes range from about 1 to about 20 nm; there are millions of different proteins. Biological materials are amazing: there are tough materials, "smart" materials, adaptive materials, functional materials, materials with molecular precision, hierarchical materials, and multifunctional materials. Many functionalities on the macroscale are based on functionalities on the nanoscale. The more we understand and abstract deep principles of biology on these length scales, the more successful can the biomimetic method transfer knowledge from materials, structures, and processes in living nature to engineering, for independent technological applications and devices.

With increasingly powerful microscopes, researchers have started to see amazing order, structure, and functionalities of biological materials, down to very small scales. Biomolecular "machines" such as the ribosome, built with atomic precision (Yusupov et al. 2001), powerful composites such as the Abalone shell (Smith et al. 1999) or the crystal eyes of brittle stars (Aizenberg et al. 2001), biomineralized beautifully structured little gems such as diatoms (Gebeshuber and Crawford 2006, Round et al. 1990/2007), optimized biotribological properties, for example, decreasing the friction coefficient to numbers so low that lubrication engineers are amazed (Gebeshuber 2007) and functional surfaces with nanoscale properties responsible for exciting tricks such as increased antireflective properties (Stavenga et al. 2006) or iridescent coloration in plants and microorganisms based on nanostructures (Gebeshuber and Lee 2012) are just some examples for the properties of organisms that are also interesting for engineering.

Currently, merging of nanoscience and nanotechnology with the life sciences, especially biology, biotechnology, biomimetics, nanomedicine, genetic engineering, and synthetic biology, can be recognized (see, e.g., Bainbridge 2007, Chen and Ho 2006, Ulvick 2010). This new and emerging field with enormous creative potential is called nanobioconvergence.

Andreas Lymberis from the European Commission, Information Society and Media Directorate-General, describes converging micro- and nanobiotechnologies toward integrated biomedical systems as

> research and development at the convergence of microelectronics, nano-materials, biochemistry, measurement technology and information technology that is leading to a new class of biomedical systems and applications, e.g., molecular imaging, point of care testing, gene therapy and bionics (including on and inside the body sensors and other miniaturised smart systems) which are expected to revolutionise the healthcare provision and quality of life. In particular they are expected to identify diseases at the earliest possible stage, intervene before symptomatic disease becomes apparent and monitor both the progress of the diseases and the effect of intervention and therapeutic procedures.
>
> **Lymberis (2008)**

Nanobioconvergence is an emerging field, and no rigid definition has been established yet. One potential definition is the following: "Nanobioconvergence denotes the merging of life sciences, especially biology and biotechnology, with nanoscience and nanotechnology, focusing on the technical output from the connections of these particular fields as well as on the unified opportunities and challenges they present to human nature and our values" (Gebeshuber et al. 2013). Biotechnology (genetic engineering, engineering of proteins, etc.), bionanoscience (focusing on molecular building blocks of living cells), and biomimetics form important constituents of nanobioconvergence. Biomimetics can be done on many length scales, but because of the hierarchical organization of organisms, with many properties based on functionalities originating from the nanoscale, biomimetics is especially rewarding when taking into account nanoscale properties of life.

Since all these fields are currently emerging, there is still a lot of defining and categorizing going on. What one set of researchers would place in biotechnology, others categorize as biomimetics. Research toward producing spider silk is a case in point. The categories can also change with time. Sarikaya and coworkers, for example, wrote in their 2003 paper "Molecular biomimetics: nanotechnology through biology" (Sarikaya et al. 2003): "Molecular biomimetics is an emerging field in which hybrid technologies are developed by using the tools of molecular biology and nanotechnology. Taking lessons from biology, polypeptides can now be genetically engineered to specifically bind to selected inorganic compounds for applications in nano- and biotechnology." Eight years later, the group reports the fabrication of hierarchical hybrid structures using bioenabled layer-by-layer self-assembly, functional hybrid nanomaterials with well-defined hierarchical and spatial organization (Hnilova et al. 2012)—something one would nowadays rather call biotechnology than biomimetics.

Biomimetic techniques applied to nanotechnology comprise technology pull and biology push. Examples for biomimetics in nanotechnology are principles of self-assembly (Valéry et al. 2003), self-repairing materials (dynamic breaking and repair of "sacrificial" bonds) (Fantner et al. 2005), bioinspired sensors (Barth et al. 2012), mass production of nanostructures (Guozhong and Ying 2011), and artificial photosynthesis (Razeghifard 2013).

On a more abstract level, Werner Nachtigall, the doyen of biomimetics in Germany, identified 10 general principles of biomimetics that can be applied by everybody working in the field, even by people who are not (or who do not want to be) involved in biology at all (Nachtigall 2009). These principles are as follows:

1. Integration instead of additive construction
2. Optimization of the whole instead of maximization of a single component feature

3. Multifunctionality instead of monofunctionality
4. Fine-tuning regarding the environment
5. Energy efficiency
6. Direct and indirect usage of solar energy
7. Limitation in time instead of unnecessary durability
8. Full recycling instead of piling waste
9. Interconnectedness as opposed to linearity
10. Development via trial-and-error processes

Nachtigall's general principles are of high relevance for biomimetics that draws its inspiration from nanoscale properties of living matter. One example for "fine-tuning regarding the environment" is navigation in honeybees. These animals orient themselves with the help of the polarization of the skylight. Abstraction of the deep principles of polarized skylight-based navigation leads to the development of technical navigation systems (produced with micro- and nanofabrication techniques) that are completely independent from the normally used GPS systems (reviewed in Karman et al. 2012).

Biomimetics at the nanoscale has as integral parts abstraction of the principles of the investigated nanomaterials, nanostructures, and nanoprocesses, followed by principle transfer to nanotechnology. In the remainder of this section, we illustrate in two examples the technology pull and biology push methods of biomimetic nanotechnology.

Technology Pull

The Carinthia University of Applied Sciences in Austria offers the MSc course "Biomimetics in Energy Systems." One of the authors of this chapter (ICG) supervised the MSc thesis "Biomimetic potential of sponge spicules" by Ehret (2012). The work performed in this thesis shall now serve as an example for "technology pull." Bioinspired improvement of daylight-guidance systems in buildings was the problem in engineering on which the thesis is based. Glass sponges (animals) were selected as model organisms with similar "problems" in living nature. The silica spicules of glass sponges serve as light guides, providing light to the photosynthesizing microorganisms and algae that live in close association with the "glass fiber" in the interior from the sponge. Detailed description of investigations of the biological role model, the glass sponges, with tools and methods from engineering, including dynamical mechanical analysis, light transmission studies, and the propagation of ultra short laser pulses, lead to the following abstractions that can subsequently be transferred to engineering: self-assembly of metal oxides on functionalized surfaces, the manufacturing of layered organic-inorganic composites with enhanced mechanical properties, and the tuning of optical and mechanical properties by means of nanostructuring and hierarchical architecture. Application of these abstractions in construction of daylight-guidance systems shall yield more conveniently illuminated workspaces in offices proof (Figure 31).

Biology Push

One example for successful "biology push" is nanoscale structures on moth eyes (Figure 32). The eyes of certain moths are covered with nipple-like arrays, which basic biological research revealed to be antireflective (Vukusic and Sambles 2003). The nipple array gradually matches the optical impedance of one medium with that of its neighbor across the interface. Such a property is of paramount interest in engineering applications, for example, for lens surfaces of camera and photographic equipment. Principle transfer to engineering is straightforward, since the property in question is dependent on the structure rather than on the material. Man-made similar nanofabricated structures (Reflexite™) yield amazing antireflective properties in a wide bandwidth, from 400 to 700 nm (Boden and Bagnall 2006, Figure 32).

Reverse Biomimetics

Prominent examples for reverse biomimetics at the nanoscale remain to be seen. Nevertheless, there is a considerable potential for such examples. Though not in the realm of reverse biomimetics, the discovery of the mechanism of ATP production in mitochondria can serve as an illustration. ATP is a universal carrier molecule of energy in organisms. Peter D. Mitchell proposed the chemiosmotic theory to explain how ATP production could work, for which he received the Nobel Prize. For the production of ATP, an electrochemical (proton) gradient across the membrane of the mitochondrion was proposed. Experiments to support this theory were performed by Racker and Stoeckenius (1974). They artificially "built" vesicles that contained ATPase (the enzyme that catalyze the decomposition of ATP into ADP and a free phosphate ion) in their membranes and through some other means they provided for a proton gradient. The arrangement of these components turned out to be causally sufficient to explain the processes in the organism (Weber 2005). Similarly, one can think of future examples where, by building of biomimetic nanoproducts, knowledge can be gained in biology.

METASCIENTIFIC CONSIDERATIONS

In this section, we deal with further considerations that are deemed important when describing biomimetics in nanotechnology: the goal and future of nanotechnology, ethical, legal, and social issues (leading to governance and risk research) and educational as well as accessibility issues in an age of converging technologies.

According to the Foresight Institute (Palo Alto, California), the goal of nanotechnology is "to improve our control over how we build things, so that our products can be of the highest quality [...] while causing the lowest environmental impact." (Foresight Institute 2015). However, it needs to be ensured that nanotechnology that is intended to cause the lowest environmental impact is not only upfront "green" with negative side effects on ourselves, further organisms, and the environment. Some human actions and technological developments might

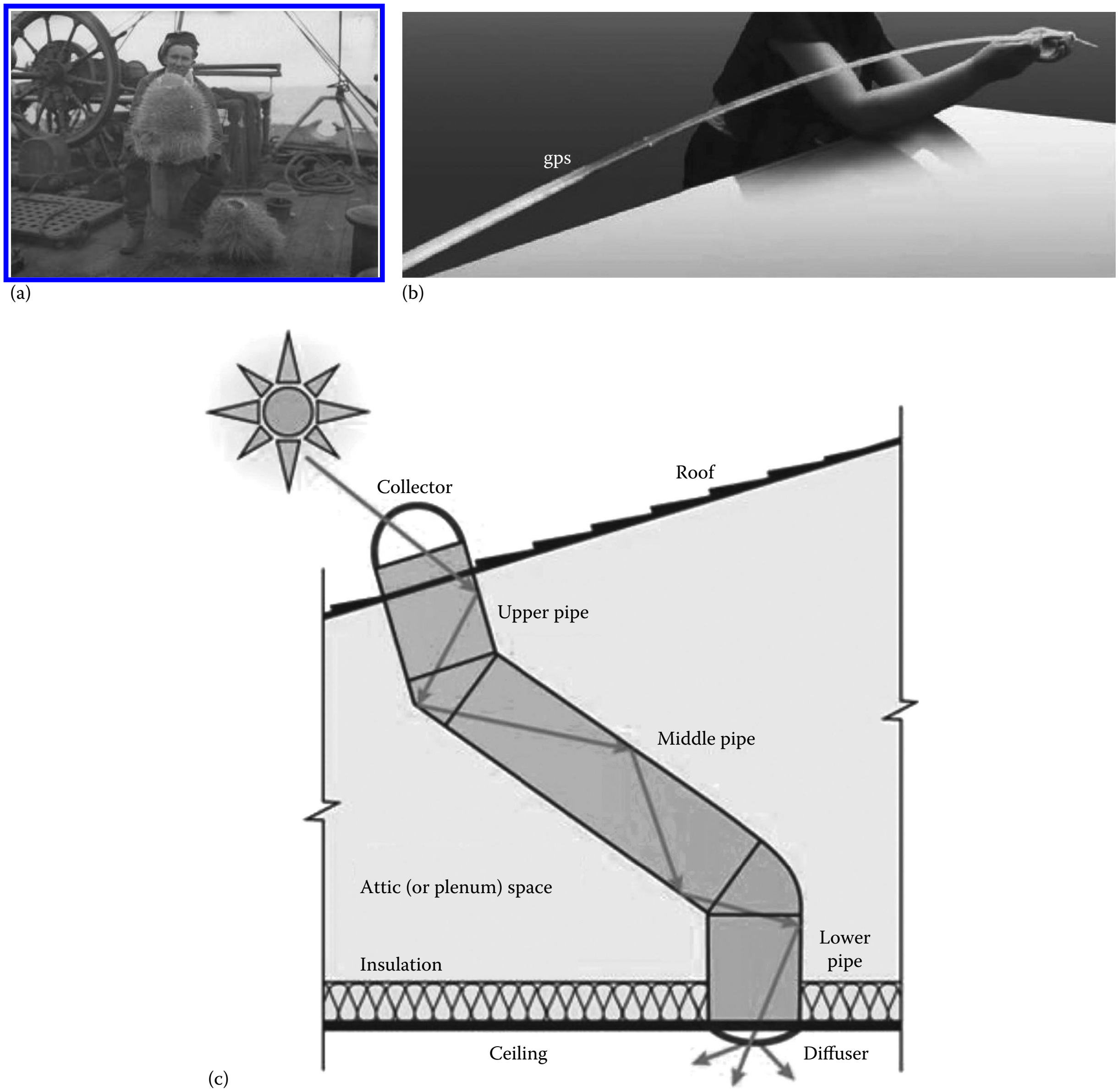

FIGURE 31 (a) A member of the 1910–1913 British Arctic expedition with a glass sponge. Some glass sponges have hydrated silica spicules that are 3 m long. Based on functionalities on the nanoscale, such spicules can be very effective fracture-resistant light guides. (Copyright Ponting Collection, Scott Polar Research Institute, Cambridge, U.K., http://www.spri.cam.ac.uk/.) (b) The largest biosilica structure on Earth: the giant basal spicule from the deep-sea glass sponge *Monorhaphis chuni*. (Reproduced from Wang, X. et al., *Evid. Based Compl. Altern. Med*., 540987, 14, Copyright 2011. With permission.) (c) Principle of daylight guiding in buildings. (Copyright Dr. Aziz Laouadi, National Research Council Canada, Ottawa, Ontario, Canada.)

have short-term benefits on the environment, but come with unforeseeable long-term effects that are hard and impossible to predict for the complex system we are all embedded in.

The progress of nanoscience and nanotechnology is accompanied by important ethical, health, environmental, and social issues. Because of the huge envisaged impact of science and technology on society, increasingly also social scientists and technology assessment specialists deal with nanoscience and nanotechnology. Prospects, problems, and potential risks require focused consideration by third parties such as parliaments, NGOs, sociologists, philosophers, insurance companies, law enforcement agencies, or scientific researchers from other fields. Technological, environmental, societal, health, and safety issues must be addressed in research, societal studies, regulatory measures, and government policies (Holsapple et al. 2005, Holsapple and Lehman-McKeeman 2005, Huber 2010, Powers et al. 2006, Thomas and Sayre 2005, Thomas et al. 2006a,b, Tsuji et al. 2006).

Societal implications of nanoscience and nanotechnology should be judged using a balanced approach between the potential achievements (leading to envisioned societal benefits) and potential hazardous consequences (which could be a combination of unexpected benefits and risks) (Roco 2003).

"Futures" in terms of visions, expectations, scenarios, fears, and hopes increasingly dominate science outreach and the

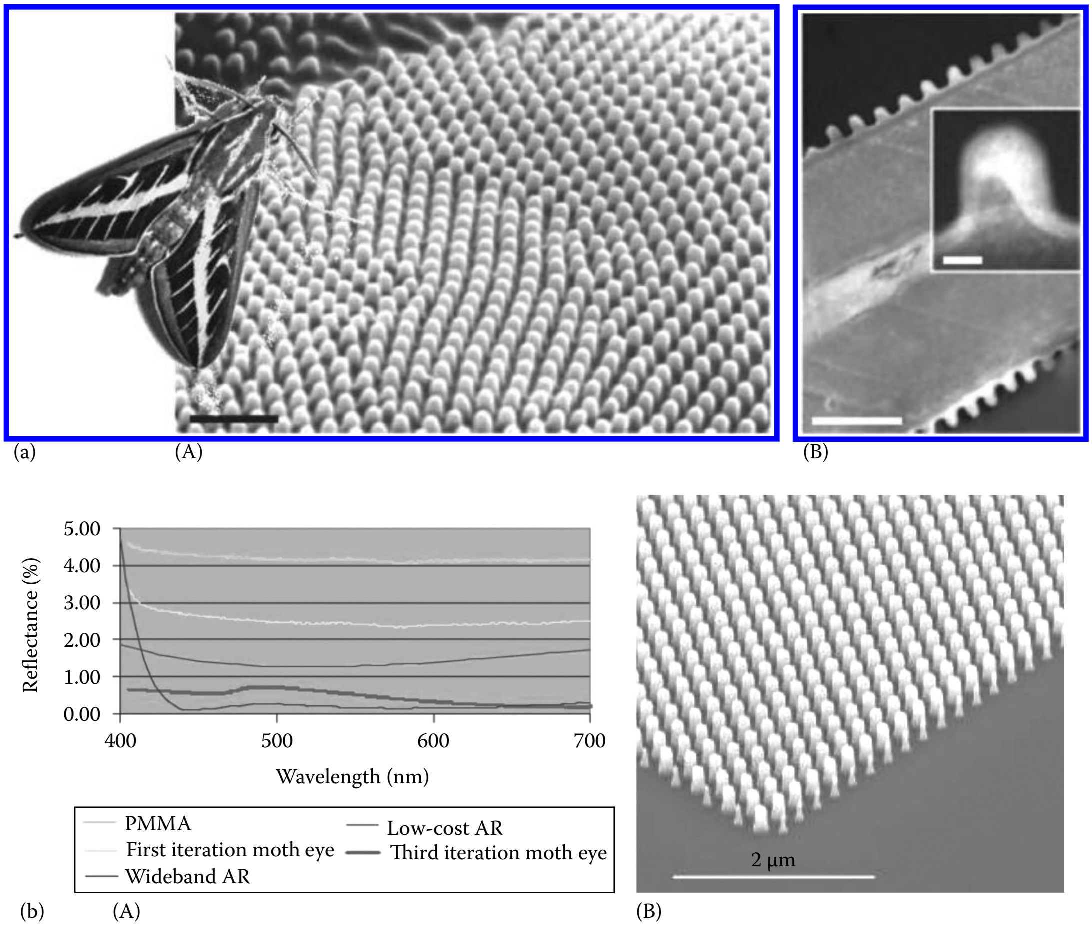

FIGURE 32 Antireflective surfaces on moth eyes (a) and the respective engineered biomimetic antireflective structures (b). (a): (A) SEM of a moth eye, showing nipple-like structures. *Inset*: Moth. Scale bar, 1 μm. (B) Similar structures on transparent wings of hawkmoths. Scale bar, 1 μm. *Inset*: Single nipple. Scale bar, 100 nm. (b): (A) Reflectance measurements on engineered antireflective surface structures. For the surface called "third iteration moth eye," reflectance is below 1% for the whole spectrum that is visible to humans. (B) Biomimetic structure, machined in silico. Scale bar, 2 μm. (a: Reproduced by permission from Macmillan Publishers Ltd. *Nature*, Vukusic, P. and Sambles, J.R., Photonic structures in biology, 424, 852–855, Corrigendum in *Nature*, 429, 680, Copyright 2003; b: Boden, S.A. and Bagnall, D.M., Biomimetic subwavelength surfaces for near-zero reflection sunrise to sunset, *Proceedings of the Fourth IEEE World Conference on Photovoltaic Energy Conversion*, Waikoloa, HI, pp. 1358–1361, 2006 © IEEE.)

drive and motivation of scientists (Grunwald 2007). Futures are socially constructed. Especially concerning nanoscience and nanotechnologies, the ongoing debate is very much a debate about futures. The visions for the future of nanotechnology have a wide bandwidth, ranging from "expectations of salvation and anticipations of paradise" (Grunwald 2010) to the announcement of the "ultimate catastrophe" (Grunwald 2010)—both extremes being based on the same futuristic technical ground.

The high degree of interdisciplinarity in nanoscience and nanotechnology poses a grand challenge as well as provides great opportunities to today's mainly specialist scientists.

To fully exploit the potential of biomimetics in the age of nanotechnology, scientists and engineers will have to substantially change their ways of thinking, especially on the level of fundamental research and education (Casert and Deboelpaep 2006, Gebeshuber and Majlis 2010, Roco 2002). Still, many researchers use for their research on a specific field in nanotechnology just the instruments they or their close collaborators have at their disposal, which are not always the best-suited ones. We have to move from tool-based nanotechnology to understanding-based nanotechnology. Martin Rees from Trinity College in Cambridge describes in his foreword to James Lovelock's 2010 book the current way of doing science as "the specialized quasi-industrial style in which most research is conducted" (Rees 2009). In such a way, true interdisciplinarity cannot be obtained. Interdisciplinary scientific principles and concepts that allow specialist scientists to understand complex phenomena need to be developed toward a unification of science (Roco and Bainbridge 2002). To allow for proper, accessible organization of knowledge, the specialist results that currently appear in increasingly specialist journals need to be rearranged and connected across fields (Gebeshuber and Majlis 2010).

CONCLUSIONS AND OUTLOOK

One of the paramount advantages of the biomimetic method as opposed to other innovation methods in nanotechnology is that we have biological "best practice" examples and know that they work. However, due to the integrated multifunctionality of biological materials, structures, and processes, it might sometimes be hard to identify the respective principles responsible for one single technological aspect that we want to transfer to research and development. In the biomimetic method applied to nanoscience and nanotechnology, we have the option to go along two roads: either to take the typical Western science approach and try to dissect the best practice models in living nature to various single, unrelated properties, some of which may be highly intriguing and successful for immediate application in common products, but that might come with unintended long-term effects, or to take a more holistic approach and appreciate the best practice models as a whole, trying to develop a deep understanding why life as we know it has developed the way we currently experience it and to develop a kind of engineering and way of *managing* resources that is closer to the way nature does it—biomimetic nanotechnology with the strive for sustainability.

Organisms show us, for example, a completely different way of resource "management" as opposed to the one we currently have in engineering and construction. They predominantly use water-based chemistry, are subject to limits and boundaries, and are in a state of dynamic nonequilibrium. They are locally attuned and responsive (they harvest locally, use common materials, etc.), integrate cyclic processes via feedback loops, cross-pollinate and mutate, and are resilient (diverse, decentralized and distributed, redundant) (Biomimicry 3.8 2014).

Biomimetics is perhaps a small but probably significant method, because the role models that can be found in living nature have been tested in evolution since billions of years and promise great nanoscience and nanotechnology-based innovations. To sum up, biomimetics in nanotechnology has great potential for exciting nanoscience and nanotechnology-based innovations.

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Nanotribology: Green Nanotribology and Related Sustainability Aspects

Ille C. Gebeshuber

CONTENTS

INTRODUCTION

Man-made machines on all length scales dominate current human lives. Technology and our current ways of dealing with resources, the transport of materials and products, manufacturing of products, and finally the disposal or reuse or recycling of products are increasingly getting green and, even more so, aim at sustainability.

People have realized that we live on a planet with boundaries, and our approaches have changed accordingly. Tribology is represented in most machines, since most machines are devices with moving parts, interacting parts in relative motion—and thereby tribosystems. With the recent rise of micro- and nanoscale technologies, micro- and nanotribologies are increasingly important and need to be included in green technology approaches. Even more so given the great future that is forecasted for nanotechnology, for which nanotribology is an enabling technology.

Green technology is understood as technology that is "better than currently used ones" or technology "regarding green applications" (such as renewable energy). Such an understanding of *green* is different from the understanding of *sustainable*, which is a more holistic concept. The technology of palm oil–based engines is a simple example illustrating the difference between green and sustainable technology. It is green technology, because such engines use vegetable oil rather than fossil fuels, and thereby have a closed carbon circle, but it is not sustainable technology, due to the usage of a substance as fuel that can also be used as cooking oil (feeding the needy) and due to the contribution of oil palm plantations to the destruction of ancient rainforest and decrease of biodiversity (which are both complex systems influencing the living conditions of future generations). Sustainable technology complies with the principles of social, economic, and ecological sustainability. It takes into consideration also future generations and their needs and good living (Robbins 2011).

The following sections define tribology and nanotribology and subsequently introduce concepts of green technology and sustainable technology, first on their own and second as concepts related to nanotribology. This way of introduction and subsequent interweaving of previously unrelated concepts allows the reader to understand the key contributing fields and the timeline in the development of green nanotribology and related sustainability aspects, bridging historic trends and current developments, accumulating in an emerging field that increasingly gains importance.

TRIBOLOGY

H. Peter Jost, president of the International Tribology Council, coined the word tribology in the year 1966. The word is a combination of τρίβω, tribo, "I rub" in classic Greek and the suffix -logy from -λογία, -logia "study of," "knowledge of." Various reports published between 1966 and 2009 for the United Kingdom and for China state that between 1% and 2% of the gross national product or gross domestic product could be saved by optimized tribology (Jost 1966, Research Report Tribologie 1976, Tribology Science Industrial Application Status and Development Strategy 2008, Zhang 2009).

In the systems science tribology, also the environment and development with time have to be accounted for; therefore, tribology and especially the emerging fields of micro- and nanotribologies (which are close in scale of action to the functional units of the green and in most cases sustainable living tribosystems) are well suited for the development and successful implementation of green and sustainable concepts.

NANOTRIBOLOGY

The term "nanotribology" was introduced in the year 1991 by Krim and coworkers in the scientific journal *Physical Review Letters* with their study on atomic scale friction of a krypton monolayer (Krim et al. 1991). Nanotribology denotes the study of tribologically interesting materials, structures, and processes with methods of nanotechnology (e.g., high-resolution microscopy). This field is of utmost importance to tribology in general, because the real area of contact between two surfaces can be very small: Rigid surfaces, for example, only touch at asperities, where extreme conditions can appear. Since the late 1980s, measurement methods have been established and are now well introduced to the scientific and engineering community that allow to obtain data on interactions that take place on such a small scale. Prominent examples for such measurement devices are scanning probe microscopy and nanoindentation techniques that can probe interactions on smallest scales (subnanometer distances, one atom thin separations, monomolecular lubricant layers). Atomic force Kelvin probe microscopy is, for example, used for the measurement of surface charges, and friction force microscopy can measure stick–slip interactions of single atoms with a crystalline surface. Because of the inherent connection of the macro- via the micro- to the nanoscale, the fields of micro- and nanotribology are of relevance for tribology at all scales (Tomala et al. 2013). One example are hip implants, where nanoscale roughness can dramatically influence the formation of bacterial biofilms on implant surfaces inside the human body, thereby increasing the risk of inflammation and necessity of another surgery. With the development of micro- and nanomachines (such as microelectromechanical systems [MEMS] and nanoelectromechanical systems, such as the acceleration sensor in airbags or nanoresonators), these fields are increasingly getting attention (Bhushan 2008). Important application fields of nanotribology are molecular dynamics studies, MEMS, hard disks, and diamond-like carbon research (Elango et al. 2013).

GREEN TECHNOLOGY

Technological advancement has for a long time been directly connected with human development. The late Professor Gustav Ranis, Frank Altschul Professor Emeritus of International Economics at Yale, for example, states that "human development, in combination with technology, yields economic growth which, in turn, is necessary to generate further advances in human development" (Ranis 2011). However, recently, this view started to change. Planetary boundaries (Rockström et al. 2009) and depletion of resources, combined with the knowledge that human technological, industrial, and further activities alter and change the Earth, in many cases not for the better, leading to a new view in which technological advancement is not seen anymore as directly correlated with an improvement of the human condition—it is now clear that besides technology, the society and the environment also need to be integrated. The planetary boundaries concept (Figure 529 and Table 127) introduced by Johan Rockström, the executive director of the Stockholm Resilience Centre, and coworkers in *Nature* in 2009 and further elaborated in a report to the club of Rome (Wijkman and Rockström 2012) is a new approach to defining biophysical preconditions for human development: they define the safe operating space for humanity with respect to the Earth's system. Earth is a complex system full of interdependencies and interconnectedness that reacts in nonlinear, often abrupt ways, and human actions are the main driver of current global environmental change. We rely on the relative stability of this system and many of its subsystems (such as the monsoon system).

Green technology is defined as technology with less impact on the environment than traditionally used technology and as technology that contributes to green applications such as renewable energy (for example to friction and wear issues in wind turbines). Keywords regarding green technology comprise life cycle assessment, green manufacturing, ecological design, green chemistry, industrial symbiosis (employs principles of ecological systems to industrial systems), ecological modernization (true green technology, disruptive technologies, e.g., new bioinspired approaches without the use of plastics or metals), and integrating concepts and frameworks at the interface of technology, society, and the environment (Robbins 2011).

Si-wei Zhang, past president of the Chinese tribological society, introduced green tribology as an international concept in the year 2009. Green tribology is the science and technology of tribological aspects of the ecological balance and their influence on the environment and living nature (Nosonovsky and Bhushan 2010, Nosonovsky and Bhushan 2012). Tribology must proceed in consensus with the most important worldwide rules and regulations concerning the environment and energy.

SUSTAINABLE TECHNOLOGY

The concept of "green" is not the same as the concept of "sustainable." Green refers to "better for the environment than conventional" or "related to green applications." The concept of sustainability emerged in the 1980s, when the United Nations published the Brundtland report (World Commission on Environment and Development 1987) and defined sustainable development as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs." The Brundtland report states: "In essence, sustainable development is a process of change in which the exploitation of resources, the direction of investments, the orientation of technological development, and institutional change are all in harmony and enhance both current and future potential to meet human needs and aspirations." Sustainability is now a widely used word, and depending on which group uses it, it can denote very different concepts. Here, in this chapter, sustainability is used in its original definition

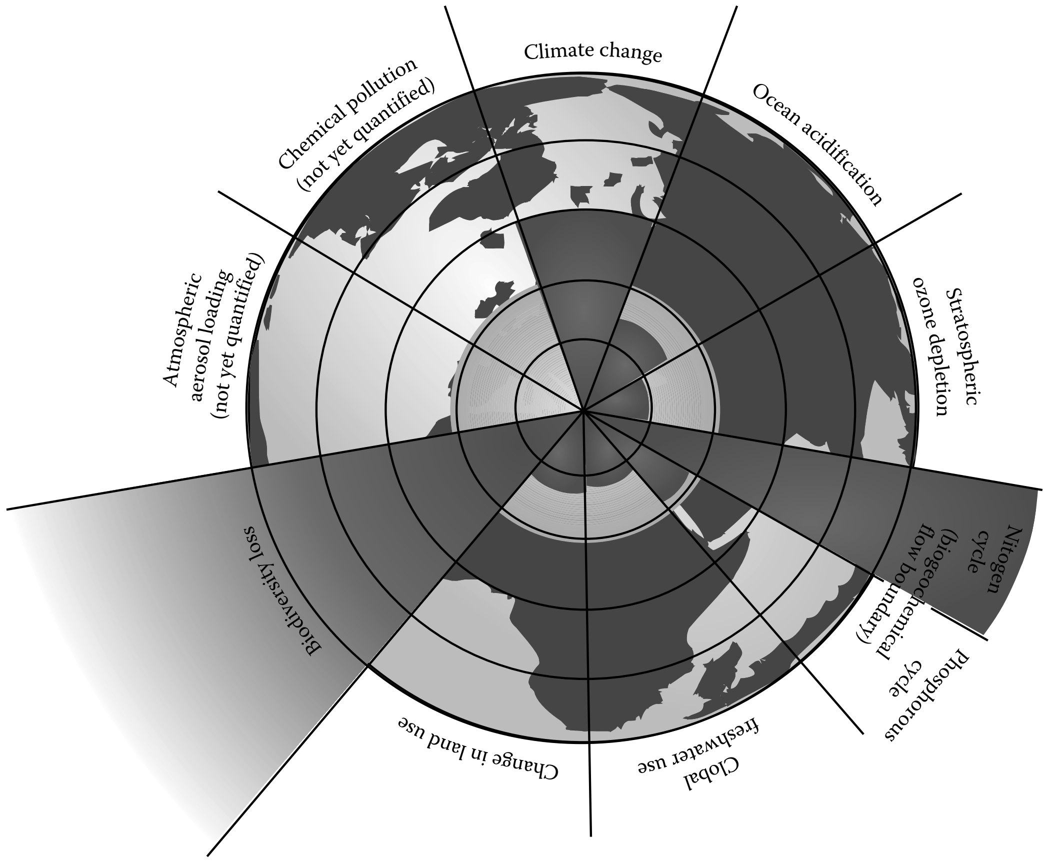

FIGURE 529 The planetary boundaries for Earth (Rockström et al. 2009). Inner circular shading: safe space. Wedges: estimates for the current position. Note that the boundaries in three systems (rate of biodiversity loss, climate change, and human interference with the nitrogen cycle) have already been exceeded. Image Copyright (2009) Nature Publishing Group. Reproduced with permission.

from the Brundtland report and thereby related to economic well being, environmental protection, and social equality.

Examples for sustainable technologies with relevance for tribology are alternative fuels (such as biodiesel, bioalcohol, nonedible vegetable oil, and nonfossil methane and natural gas), electric cars, energy recycling, environmental technologies (such as renewable energy, water purification, air purification, sewage treatment, environmental remediation, solid waste management, and energy conservation), hydropower, manure-derived synthetic crude oil, soft energy technologies, water power engines, wave power, and windmills. For more in-depth information on the connections and interdependencies of technology, globalization, and sustainable development, the reader is referred to Ashford and Hall (2012).

GREEN NANOTRIBOLOGY

Green nanotribology is green technology dealing with friction, adhesion, wear, and lubrication of interacting surfaces in relative motion at the nanoscale. A smart combination of mechanical, energetic, and chemical approaches, combined with optimum designed materials, and minimized stresses to the environment and biology, paths the way toward green nanotribology.

Green nanotribology includes biomimetic tribological nanotechnology; sustainable control of friction, adhesion, wear, and lubrication on the nanoscale; environmental aspects of nanoscale lubrication layers; environmental aspects of nanotechnological surface modification techniques; and nanotribological aspects of green applications such as artificial photosynthesis. Green nanotribology shall be able to provide technical support to the preservation of resources and energy.

The components of green nanotribology (Gebeshuber 2010, Gebeshuber 2012) are nanostructured surfaces, nanoagents (ingredients, additives, products of the additives, and by-products that appear in the system after the technological application), and nanoprocesses (see Table 126).

GREEN NANOTRIBOLOGY AND RELATED SUSTAINABILITY ASPECTS

Tribologists are already used to the inherent interconnectivity of various aspects of their profession, and it is easier for them to adopt new holistic concepts such as green and sustainable as opposed to most other people working in technology fields.

In 2006, the eminent tribologist Prof. Wilfried Bartz, published an article in the scientific journal *Tribology International* on Ecotribology. He relates environmentally acceptable tribological practices to saving of resources of energy and reducing the impact on the environment (Bartz 2006). In a now classic

TABLE 126
Nanotribology Components, Their Importance, and Points to Address for Going Green

Nanotribology	Importance	Points to Address
Nanosurfaces	Medium	Nanostructured surfaces
		Hierarchical surfaces
		Material selection
		Coated materials
		Monomolecular lubricant layers
Nanoagents	High	Physical properties
		Chemical properties
		Effect on environment and organisms
		Changes of properties with time
		Changes of properties in the triboprocess
Nanoprocesses	Medium to low	Energy efficiency
		Share between process relevant energy, destructive energy, and waste as well as reusable energy
		Effectiveness of reusing process energy

Source: Gebeshuber, I.C., Green nanotribology and sustainable nanotribology in the frame of the global challenges for humankind, in: *Green Tribology—Biomimetics, Energy Conservation, and Sustainability*, Bhushan B. (ed.), Springer, Heidelberg, Germany, 2012, pp. 105–125.

illustration, the ecobalance tree, Bartz mentions important parameters that need to be taken into consideration in the development of ecotribology: the raw material, its transport, the production of products using materials, the transport of these products, the usage, and the disposal. Important aspects are the exploitation of resources, waste management, emissions, recycling, combustion, and reusage.

Sasaki's 2010 article on environmentally friendly tribology (Ecotribology) in the *Journal of Mechanical Science and Technology* focuses mainly on progress through surface modification (Sasaki 2010).

Tzanakis and coworkers highlight future perspectives of sustainable tribology in their 2012 article in the *Renewable and Sustainable Energy Reviews* (Tzanakis et al. 2012). They present three interesting case studies from diverse areas of interest in tribology (micro-CHP (combined heat and power) systems, slipways for lifeboats, recycled plastics for skateboard wheels) and perform tribological analyses and sustainability considerations.

Gebeshuber introduced sustainable nanotribological systems based on the sustainability concept of design lectures from living nature, the principles of life as introduced by the Biomimicry Guild in 2009 (Gebeshuber 2012, Figure 530). The six basic categories are "survival because of evolution" (in the context of sustainable nanotribology, this means continuous incorporation and anchoring of information), resource efficiency regarding material and energy (closed tribosystems, recycling and reuse of substances and waste energy), adaptation to changing conditions (reactive nanosurfaces, nanoagents, and nanoprocesses that change depending on the environment and that are used in as small amounts as necessary), integration of development with growth (in the context of sustainable nanotribology, this means achieving a balance between development and growth), responsiveness and being locally attuned (tribological systems not as good as possible, but as good as necessary, with additional benefits regarding energy savings and environmental compatibility), and the usage of life-friendly chemistry (water-based chemistry, green chemistry—one of the basic requirements of green nanotribological systems) (Table 127).

OUTLOOK

Green and sustainable nanotribologies are currently relatively small fields that act as enabling technologies for nanotechnology in general. Optimized nanotribological systems where from the very beginning concepts of sustainability are integrated can pave the way for sustainable nanotechnology

FIGURE 530 Green and sustainable nanotribologies, word cloud constructed from Gebeshuber 2012.

TABLE 127
Contributions of Green Nanotribology to Address Issues Arising from the Nine Planetary Boundaries

Planetary Boundary	Green Nanotribology Solutions
Climate change	Energy materials with optimized tribological performance; reduced information and communication technology (ICT) global greenhouse gas emissions by optimized micro- and nanomechanics; less CO_2 waste of machines due to optimized tribology (less fuel consumption in production and use).
Rate of biodiversity loss	Less consumption of resources via optimized nanotribology in production and use allows for less deforestation and more places for wildlife to thrive.
Interference with the nitrogen and phosphorus cycles	Optimized nanotribosystems with reduced NO_x and phosphate emissions.
Stratospheric ozone depletion	Usage of nonflammable, non-ozone-depleting solvents.
Ocean acidification	Less CO_2 waste of machines due to optimized tribology (less fuel consumption in production and use).
Global freshwater use	Optimized nanotechnological desalination processes, wastewater treatments, and sewage treatments.
Change in land use	Optimized nanotribological systems for optimized land use (more efficient production, storage, novel batteries that take less space, etc.).
Chemical pollution	Reduced lubricant spillage by usage of molecularly thin lubricant films instead of bulk lubrication.
Atmospheric aerosol loading	Optimized machines giving off less small wear particles and less polluting exhaust fumes.

Note: See Figure 529.

that improves the human condition and the condition of the environment around us and that provides a technological environment that grants freedom to pursue long-term social and economic development.

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