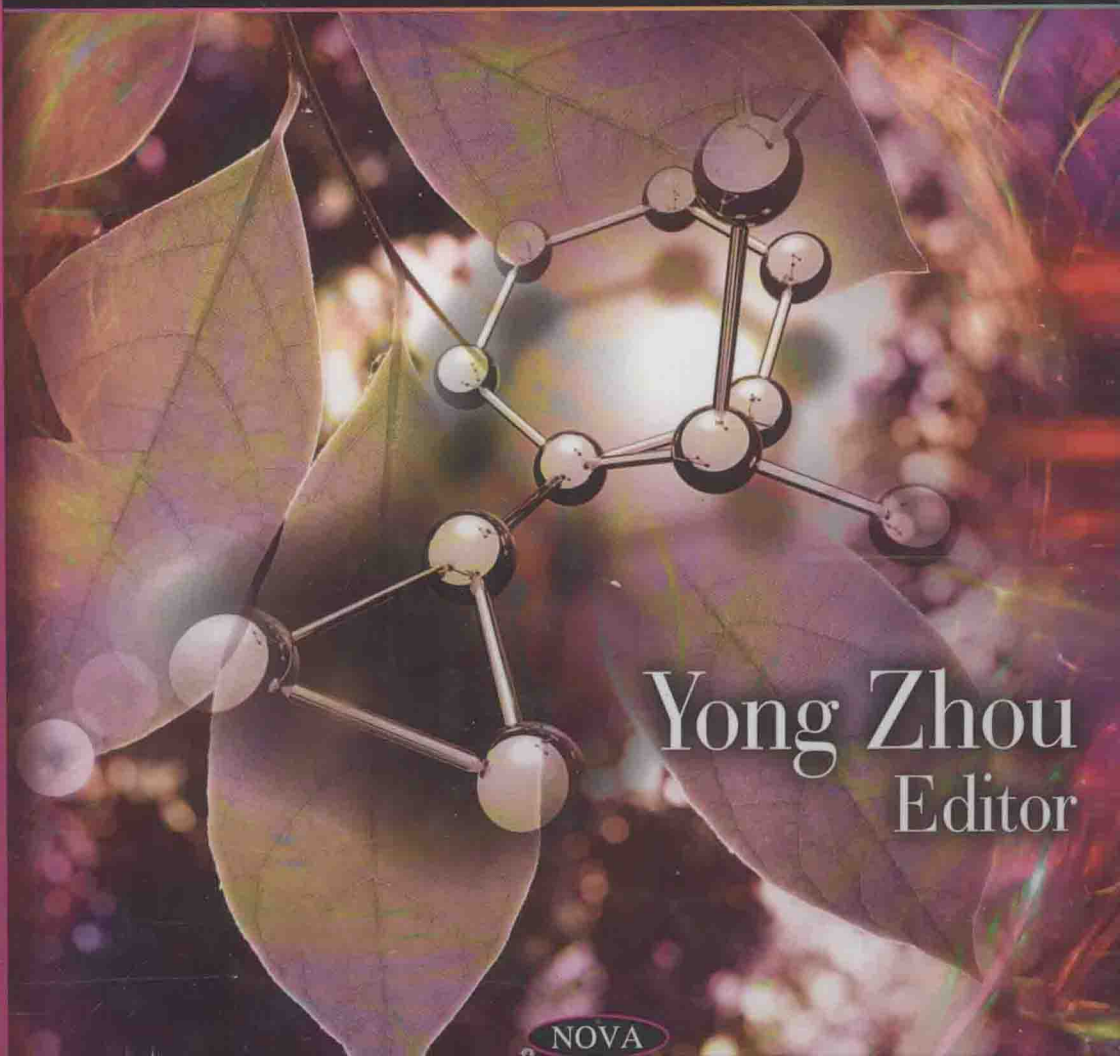


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Bio-Inspired Nanomaterials and Nanotechnology

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Yong Zhou
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NANOTECHNOLOGY SCIENCE AND TECHNOLOGY SERIES

BIO-INSPIRED NANOMATERIALS AND NANOTECHNOLOGY

YONG ZHOU

EDITOR



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PREFACE

Nanoscience is a rapidly evolving field of studying and working with matter on an ultra-small scale, which was invented late in the twentieth century. Learning from bio-systems in Nature, scientists began to design experiments to specifically couple biology with nanofabricated materials, devices and tools. Such bio-inspired nanoscience utilizes biological processes, shape, chemical and physical functionality of biomolecules for atom-levelly controllable fabrication of advanced materials with extreme precision.

This book presents our current knowledge and understanding of bio-inspired nanoscience by a collection of eleven impressive chapters, covering several remarkable aspects. Chapter I by Anwu Xu summarizes the developments of biomimetic synthesis strategies of materials with specific size, shape, orientation, composition, and hierarchical organization. Jianguo Huang in Chapter II describes a so-called “artificial fossilization process” developed to achieve inorganic replicas of the biological species which possess the corresponding finest structure details and morphological hierarchies all the way down to nanometer scale. Chapter III by Noritada Kaji and coworkers surveys fundamental fabrication techniques for micro- and nanostructures on silicon and glass substrates, various approaches for biomolecule separation based on different separation mechanisms, and practical applications such as DNA separation from the aspect of “nanomaterials and nanotechnology for bio-analytical chemistry”. Chapter IV by Yue Li et al. reviews the bionic self-cleaning effect based on the superhydrophobic surfaces of hierarchical micro/nano structures fabricated with colloidal crystal techniques. Omid C. Farokhzad and coworkers in Chapter V discuss the rationale for molecularly targeting nanoparticles, the various classes of targeting ligands, the formulation of targeted nanoparticles, and highlight interesting examples from the preclinical data on targeted nanoparticle therapeutics. In Chapter VI Shuyan Gao focuses attention on the biopolymer-assisted green synthesis and properties of structured metal, semiconductor, and magnetic nanomaterials. David H. Gracias and coworkers in Chapter VII state the recent development of engineering technologies in an effort to mimic one of nature’s simplest machines: a grasping appendage which opens or closes on-demand. Chapter VIII by Julio A. Camarero reviews the progress of new chemical and biological technologies for the site-specific immobilization of proteins onto inorganic materials and their potential applications to the fields of micro and nanotechnology. In Chapter IX by Gebeshuber et al., a variety of biological systems are introduced: *Bacillus subtilis*, the green alga *Euglena gracilis*, diatoms

and red blood cells. Subsequently results of bionanotechnological research performed (by physicists) on these systems are presented. In the next step, the systems and the results are discussed with an architect, resulting in a multitude of ideas, possible approaches, experiments and projects. The layer-by-layer (LbL) self-assembly method, which is based on the stepwise electrostatic self-assembly of oppositely charged species, has emerged as a promising and versatile approach to the fabrication of functional core-shell particles with well-defined shell structures. In Chapter X, Aimin Yu et al. highlight their recent work on the preparation of biocompatible colloidal systems via biofunctionalization of mesoporous silica particles with nano-structured shell composition via the LbL self-assembly technique, and their applications in ultra-sensitive immunoassay and biomolecule encapsulation. Xia Tao and coworkers in Chapter XI describe the fabrication of hollow biopolyelectrolyte microshells with the LBL method, and key properties of these microshells including their mechanical stability and potential applications in drug loading/release and pollutant remediation.

In working on this book, the editor had great pleasure interacting with the authors. He is grateful to all of them for their friendly and competent co-operation. Thanks are due to the publisher for expedient support. We sincerely hope that this book will provide researchers in these fields with newest developments in this rapidly evolving field for advancing research. We also wish to stimulate the next generation of breakthroughs of the bio-inspired nanosciences, which will further enrich human life.

Yong Zhou
Nanjing, China
September, 2009

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Chapter I

BIOMIMETIC MINERALIZATION AND MESOCRYSTALS

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ABSTRACT

Self-assembly into highly ordered superstructures and control over the shape and the size of inorganic materials is an important character of natural growth phenomena. In biological systems, the results of long-term evolutionary optimization processes are intimately related to specific functions. Bio-inspired materials synthesis is a powerful strategy for the synthesis of advanced materials with complex shape, hierarchical organization and controlled size, structure and polymorph in aqueous environments under ambient conditions. Increased understanding of biomineralization mechanisms has greatly enhanced the possibilities of biomimetic mineralization and template synthesis approaches. Bio-inspired materials with complex structures and advanced functions always attract attention because of their unique properties, which have paved the way to many potential applications. Organic templates such as biopolymers and synthetic amphiphilic polymers can be employed to understand the interaction of the organic matrix with the developing inorganic crystals at a molecular level and to address the question which factors lead to the remarkable crystallographic orientation of the crystalline phase, crystal growth and nanoparticle assembly, which is often observed in biomineralization. Clear evidence has shown that crystallization does not necessarily proceed along the classical crystallization process, which is the attachment of ions/molecules to a primary nanoparticle forming a single crystal, instead, crystallization can also proceed along a particle mediated self-assembly pathway. Mesocrystal is a

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quasi-single crystal consisting of ordered assemblies of small, anisotropic, and vectorially aligned nanoparticles, thus forming an entirely new class of porous metamaterials through mesoscopic transformations and nanoparticle precursors. Such composite crystals are of considerable interest to a broad range of disciplines including materials chemistry and life science as well as crystallization-related fields in general. It has been found that nanoclustered crystal growth, mediated by organic templates, is a basic characteristic of biomineralization that enables the formation of composite materials with elaborate morphologies and structures. During the past decade, exploration as well as application of these bio-inspired synthesis strategies has led to novel materials with specific size, shape, orientation, composition, hierarchical organization and assembled superstructures. This overview tries to capture the concepts and recent progress in this rapidly developing field, and prospects for the future in this field has been discussed.

1.1. INTRODUCTION

Learning from nature is a constant principle for there are numerous mysterious features in nature, which have developed over millions of years of evolution and will inspire us to develop new functional materials. Bio-inspired and biomimetic concepts borrowed from Nature have been developed for synthesizing novel functional materials such as bio-inorganic materials, bio-inspired, multiscale structured materials, bio-nanomaterials, hybrid organic/inorganic implant materials, and smart biomaterials [1]. These bio-inspired, smart materials are attracting much interest because of their unique properties, which have paved the way to many potential applications. Interfaces between biomolecules and inorganic materials have been the focus of research in various fields such as biochemistry, materials chemistry, biomedicine and bionanomaterials.

Materials with complex shapes and interface functions always attract attention and fascination. In view of the huge time frame Nature had to optimize and perfect functional materials, it is obvious that scientists are highly interested to develop synthetic strategies that mimic these natural processes. Especially promising materials in this respect are biominerals, which combine complex morphology over different length scales with superior materials properties and environmentally friendly synthesis and biocompatibility. This makes them very attractive archetypes for materials chemists. To mimic the synthesis of these materials, the main purpose is not to simply emulate a particular biological architecture or system, but to abstract the guiding principles and ideas and use such knowledge for the preparation of new synthetic materials and devices. Based on these concepts a rapidly developing research field has evolved, which can be summarized as bioinspired or biomimetic materials chemistry [2]. The creation of superstructures resembling naturally existing biominerals with their unusual shapes and complexity, is meanwhile an important branch in the broad area of biomimetics [3]. During the past decade, exploration as well as application of these bio-inspired synthesis strategies has resulted in materials with specific size, shape, orientation, composition, and hierarchical organization [4]. This chapter will summarize these developments and give some examples what can already be achieved by applying natures' strategies for biomineral synthesis. This review can not be comprehensive, therefore we have

selected some topics, those are closely mimicking biomineralization strategies. We consider biomimetic mineralization as mineralization in aqueous solutions under ambient or nearly ambient conditions borrowing strategies from biomineralization processes.

This chapter is organized into five sections. We have structured the paper in a way that first the main concepts underlying biomineralization are introduced and then, the specific examples for biomimetic mineralization are given in the following. The main contents of this review involve strategies for biomineralization, biomimetic mineralization and mechanisms, Non classical crystallization and mesocrystals, and bio-inspired functional nanomaterials. Finally, summary and outlook is discussed.

1.2. BIOMINERALIZATION

Biomineralization is the process by which living organisms secrete inorganic minerals in form of skeletons, shells, bone, teeth, magnetic iron minerals in bacteria, etc. (Figure 1) [5]. It is already a rather old process in the development of life, which was adapted by living beings probably at the end of the Precambrium more than 500 million years ago [6]. Materials found in nature combine many inspiring properties such as sophistication, miniaturization, hierarchical organizations, hybridation, resistance and adaptability [7]. Elucidating the basic components and building principles selected by evolution to propose more reliable, efficient and environment respecting materials requires a multidisciplinary research.

Biomaterials are highly organized from the molecular to the nano- and macroscales, often in a hierarchical manner, with intricate nanostructures those ultimately make up a lot of different functional soft and hard tissues (Figure 1). Under genetic control, biological tissues are produced in aqueous environments under mild physiological conditions by using biomolecules, primarily proteins but also carbohydrates and lipids. Biomolecules both collect and transport raw materials, and consistently and uniformly self- and co-assemble subunits into short- and long-range-ordered nuclei and substrates [8]. For example, magnetotactic bacteria, are able to form nano-sized, membrane-bound magnetic iron minerals, magnetite (Fe_3O_4) or greigite (Fe_3S_4), by a mineralization process with precise biological control over iron accumulation and mineral deposition [9]. The unexpected and unusual features of these biogenic magnetite crystals are not only a narrow size distribution, but above all, a diameter range of 40 ± 120 nm, which thus allocates them the highest magnetic moment. This diameter range corresponds to magnetite crystals with a single magnetic domain [10] (Figure 1f). More examples of biomaterials can be addressed as the caption in Figure 1. Whether in controlling biomaterial formation, biological functions or physical performance, biomolecules are an indispensable part of biological structures and systems. A simple conclusion is that next-generation biomimetic systems should include biomolecules in synthesis, assembly or function [11].

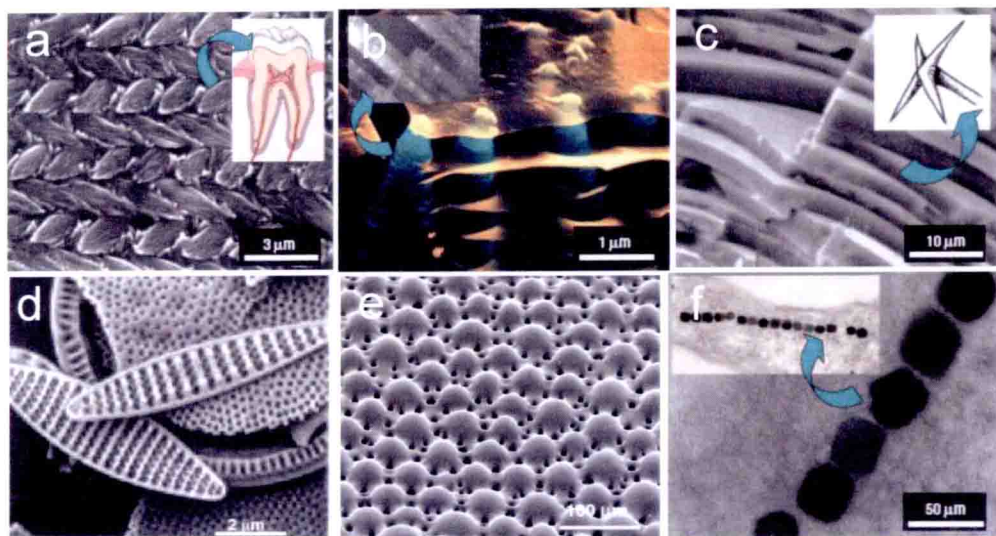


Figure 1. Representative examples of biologically synthesized complex biomaterials. (a) scanning electron microscope (SEM) image of mouse enamel. It is a hard, wear-resistant material with highly ordered micro/nano superstructure comprised of hydroxyapatite crystallites that assemble into woven rod architecture (inset: schematic cross-section of a human tooth) [12]. (b) SEM image of a growth edge of abalone (*Haliotis rufescens*) displaying aragonite platelets (blue) separated by organic film (in orange) that finally becomes nacre (mother-of-pearl). This is a layered, tough, and high-strength biocomposite (inset: transmission electron microscope (TEM) image) [13]. (c) sponge spicule (with a cross-shaped apex shown in inset) of Rosella has layered silica with excellent optical and mechanical properties, a biological optical fiber (SEM image) [14]. (d) SEM image of siliceous skeletal structures in diatomaceous earth. Actinopoda and diatoms, single-celled organisms, create amorphous siliceous units that are resting spores with highly intricate and symmetrical geometrical shapes [15]. (e) SEM of the peripheral layer of a dorsal arm plate (DAP) from *Ophiocoma wendtii* with the microlenses structures in brittlestars. Skeletal elements of echinoderms are each composed of a single crystal of oriented calcite shaped into a unique, three-dimensional mesh. *Ophiocoma wendtii* is a highly photosensitive species, and it changes color markedly, from homogeneous dark brown during the day to banded grey and black at night [16]. (f) magnetite nanoparticles formed by magnetotactic bacterium (*Aquaspirillum magnetotacticum*, inset: TEM image) are single-crystalline, single-domained and crystallographically aligned [9].

It is commonly assumed in the biomineralization field, that the remarkable biomaterials morphologies are fabricated under total control of specific biomolecules so that biomineralization is eventually a genetically controlled process, which transforms the genetically engineered organic scaffolds into soft and hard matter. On the other hand, the recent nacre retrosynthesis example [17] has already indicated that the natural biopolymers can be replaced by synthetic polymer analogues so that some of the biomineralization mechanisms are much related to physicochemical principles such as nucleation inhibition rather than specific biopolymer structures and functions. Although a protein may exhibit a complex structure, its actual function may be simple, for example, serving as a polyelectrolyte in a biomineralization process. Therefore, it makes sense to investigate, on how far physicochemical principles play a role in biomineralization. An excellent example

for this is the pattern formation in diatoms, which can be explained by a phase separation model of amphiphilic polyamines (Figure 2) [18].

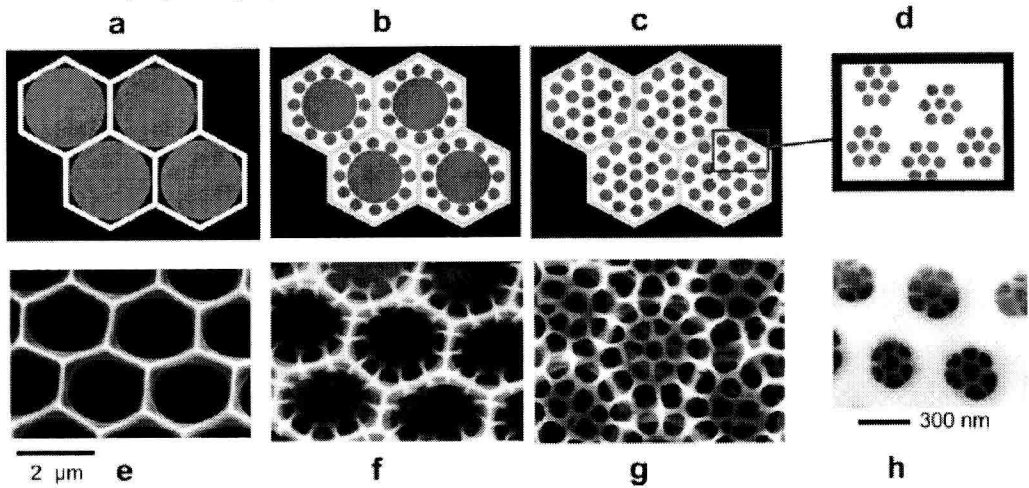


Figure 2. Schematic drawing of the templating mechanism by the phase-separation model (a–d) and comparison with the stages of the developing cell wall of *C. wailesii* (e–h). (a) The monolayer of polyamine-containing droplets in close-packed arrangement within the silica-deposition vesicle guides silica deposition. (b, c) Consecutive segregations of smaller (about 300 nm) droplets open new routes for silica precipitation. (d) Dispersion of 300 nm droplets into 50 nm droplets guides the final stage of silica deposition. Silica precipitation only occurs within the water phase (white areas). The repeated phase separations produce a hierarchy of self-similar patterns. (e–h) SEM images of valves in statue nascendi at the corresponding stages of development. Reprinted from Ref. [18] with permission of the American Association for the Advancement of Science.

In this model, amphiphilic polyamines phase separate and form an emulsion of closely packed microdroplets in a hexagonally arranged monolayer within the flat silica deposition vesicle (SDV, Figure 2a). Phase separation is induced by coordination of positively charged polyamines with phosphate, and also incorporated in the polyamine itself in form of phosphoserins [19], which acts as a cross linking agent [20].

The silica precursors in form of a polyamine stabilized sol are located at the aqueous interfaces between the microdroplets. As a consequence, upon silica formation, a honeycomb-like hexagonal framework is produced (Figure 2e). After partial consumption of the polyamines by inclusion into silica, a further segregation of the initial microdroplets into smaller droplets is assumed (Figure 2b). The newly created interfaces again serve as the template for silica deposition (Figure 2f) and a further fraction of the polyamines is consumed. This leads to a further phase separation of the polyamines into 300 nm sized droplets (Figure 2c) and silica deposition at the aqueous interface between the droplets (Figure 2g). A final phase separation of the nanodroplets into only 50 nm sized droplets (Figure 2d) with subsequent mineralization of the aqueous interface between the droplets results in the observed hierarchically hexagonal self-similar patterns. This pattern formation mechanism, fully based on a series of consecutive phase separation steps, results in a pattern, which matches that of the diatom valve of *Coscinodiscus* [18].

Above result indicates that such physicochemical principles can be transferred to biomimetic mineralization for the generation of advanced materials as summarized for the polyamine case in Ref. [21]. It will be interesting to reveal further physicochemical mechanisms in bio- and biomimetic mineralization such as the minimization of interface energies by the formation of an amorphous surface layer and growth inhibition by foreign additives/impurities [22]. These principles will make us to a deeper understanding of biomineralization processes and thus extend the toolbox of biomimetic mineralization by a transfer of biomineralization principles to the synthetic materials field.

1.3. BIOMIMETIC MINERALIZATION

Biomimetic mineralization based on the biomineralization principle of templating of inorganic structures by soft organic templates has already been transferred to materials synthetic science. Organic templates can be employed to understand the interaction of the organic matrix with the developing inorganic crystals at a molecular level and to address the question which factor result in the remarkable crystallographic orientation of the crystalline phase, which is often found in biomineralization. The templates are thus used as mimics of an oriented structural matrix in biomineralization. Importance in this respect is Langmuir monolayers as a template, because they are available with different head groups and can be compressed so that a range of regular template structures can be adjusted. There have been numerous reports on the selective nucleation of certain crystal faces under Langmuir monolayers as summarized in Refs [23], and initially, epitaxy or stereochemical resp. geometrical match between the arrangement of the charged groups of the monolayer and the ion arrangement on the nucleated crystal surface was discussed. More recently, Cavalli et al. demonstrated that flexible self-organizing β -sheet lipopeptide monolayers led to a new growth habit of calcite and thus the formation of indented calcite crystals. This study confirmed the importance of flexibility of the template in crystal oriented nucleation [24]. In addition to Langmuir monolayers, self assembled monolayers (SAM's) can also be used to investigate the influence of the functional groups and other parameters on the mineral deposition and orientation. The advantage is that the SAM's are chemically fixed to the substrate and that they can be patterned by PDMS stamping or surface lithography.

The most remarkable result with patterned SAM's was reported by Aizenberg et al. for the direct fabrication of large micropatterned calcite single crystals [25], which can be considered to be a rough mimic of the oriented single crystal calcite microlens arrays in brittlestars [16]. First, photoresist micropatterns were formed on a glass surface by photolithography. Then, the surface was coated with Au or Ag. As a very important step, a localized nanoregion of a polar alkanethiol was deposited on the surface with an AFM tip serving as a single nucleation center for calcite with a known orientation. Then, the remainder of the metal surface was coated with alkanethiols with varying length and functionality, which created a disordered surface and therefore favored the formation of amorphous calcium carbonate (ACC). First, a mesh of metastable ACC filled the interstices of the framework followed by site specific nucleation of a calcite single crystal at the deposited nucleation spot. This single crystal grew by transformation of the surrounding ACC finally leading to a micropatterned single crystal

as imaged by polarization microscopy. The micropatterned surface was found to serve for the release of stresses, water and impurities during the formation of the final crystal.

As a soft template used in biomimetic synthesis, double hydrophilic block copolymers (DHBCs) are a new class of amphiphilic macromolecules of rapidly increasing interest. They are water-soluble polymers in which amphiphilicity can be induced through the presence of a substrate or by temperature and pH changes. Their chemical structure can be tuned for a wide range of applications such as colloid stabilization, crystal growth modification, induced micelle formation. In particular, mineralization processes can be controlled by using DHBCs as inspired by biology, which have a molecular head group reacting with the metal ions and a central non-reactive part similar to proteins containing hydrophilic and mineralophilic sites [26]. Such polymers help to control the size, mineral forms, structure and assemblies of inorganic crystals. Indeed, original superstructures have been prepared, as well as aligned hydroxyapatite whiskers or mineral crystals having complex morphologies [2, 26].

More recently, a DHBC polymer with high molecular weight has been applied for the crystallization process of BaCO_3 crystals [27]. At the critical point between aggregation towards long fibres and spheres, the short nanofibers at starting pH 5.5 self-organized towards most striking dynamic ring structure patterns on the large scale. Figure 3 shows typical SEM images of the obtained quasiperiodic wave patterns grown in solution for 1 day. Light microscopy images indicate that those patterns were already formed in the aqueous solution. This periodic wave pattern has multiple centres, from which concentric rings with even spacing radiate outwards (Figure 3a), reminiscent of the target (concentric) waves in the spatially extended Belousov-Zhabotinsky (BZ) reaction. A set of coupled chemical reactions necessary for the establishment of a reaction-diffusion system could be formulated including an autocatalytic formation of a Ba-polymer complex. On the substrate, many groups of concentric rings grow at the same time and stop when merging with each other. The enlarged SEM image shows that each ring (band) is composed of short nanorods standing on the substrate instead of lying, and tending to form bundles on the substrate, which are organized into a circular pattern around the center (Figure 3b, c). It is noteworthy that the experimental window is narrow for the formation of this concentric circle pattern [27].

The periodic pattern formation in this reaction system belongs to a self-organization process, in which competition between autocatalytic particle growth and educt diffusion occurs. This concentric circle pattern is a vivid and ubiquitous phenomenon in the reaction-diffusion system. In the meantime, numerical simulations using a modified Oregonator model for the reaction-diffusion equations qualitatively agree with the experimental observations. Figure 4d shows the simulation result for the BZ reaction, similar to the experimental ring patterns. It is important to note that similar patterns can also be found in natural minerals; spiral patterns of nacre (aragonite CaCO_3) have been found on the growing inner surface of nacre [28], and in that case, screw dislocations were believed to be responsible for spiral growth of nacre.

Calcite crystals with exposed (001) faces have recently been obtained in the presence of poly(sodium 4-styrene sulfonate-*co*-*N*-isopropylacrylamide) (PSS-*co*-PNIPAAm) (Figure 4a, b) [29]. Usually, calcite is not able to expose the (001) faces because these faces are composed of only CO_3^{2-} or Ca^{2+} ions in a hexagonal orientation, respectively, and therefore are highly charged faces. Such highly charged faces would exhibit high surface energies and