The mission of our research group is to advance the design of functional and structural hybrid materials through understanding and controlling the chemical and physical interactions between the constituting components. Within the laboratory this is currently pursued along two closely related research lines that comprise “Bio-inspired Materials” and “Multiscale Materials”.

Bio-inspired Materials
Biominerals such as bones, teeth, and shells often have physical (mechanical, optical) properties, that in many cases match those of man-made materials and which derive from the high level of control over the structure, size, shape, and assembly of the constituents. A yet unfulfilled dream of many scientists is to synthesize new materials with similar advanced properties applying Nature’s biomineralization strategies. For this we must first unravel the mechanisms of biologically controlled mineral formation.

By mimicking natural systems in the laboratory we aim at obtaining insight in the principles of biomineralization, and subsequently explore these in the synthesis of novel hybrid materials. In our bio-inspired mineralization experiments we use both biogenic macromolecules such as collagen and other biomineralization proteins, but synthetic polymers and (macro)molecular assemblies such as polypeptides and Langmuir monolayers, to direct the formation of a variety of minerals, including calcium carbonate, calcium phosphate, silica, and iron oxides.

Multiscale Materials
The mesoscale structuring of materials (i.e. tens to hundreds of nanometers) determines the interactions between their different components and hence is key to many technological applications. Also in biology we find many examples in which the hierarchical organization of building blocks extends over several length scales and gives rise to advanced physical properties, tailor-made to specific such as skeletal support, light harvesting and magnetic sensing. It is clear that to orchestrate the multiscale assembly of materials with mesoscopic structure we must advance our understanding on the assembly of materials systems from smaller structural and functional units.

In our studies we combine the use of both bottom up (Self-assembly) and bottom up approaches to generate hybrid materials from polymeric, mineral and carbon based building blocks. We use advanced electron microscopic techniques to obtain information on structure formation both during the molecular self-assembly of the mesoscale building blocks, and during their colloidal self-assembly into larger, multi-micrometer scale structures. This will provide new insights in the different stages of the assembly processes, and helps us to optimize the synthesis of functional hierarchical structures.

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Unravelling the Molecular Mechanism of Collagen Mineralization

Anat Akiva

Introduction

Bone tissue is a unique composite material that provides the mechanical support of our bodies. Its basis is an organic matrix of collagen, in which extremely thin (~4 nm) crystalline platelets of apatite are embedded and aligned along the collagen fibrils. The detailed analysis of the structure of the mineralized collagen fibril has proven difficult and is still continuously refined. Understanding the process of collagen mineralization is essential for the development of treatments of bone defects and mineralization related diseases and will offer new opportunities for the design of new materials.

Project summary

Most of collagen mineralization studies use collagen that originates from different sources for in vitro mineralization. Usually, these collagen samples have no recorded history (age, clinical stage, sample treatment etc.) and the possibility to track specific proteins that are essential to the mineralization process is not achievable. Using human mesenchymal stem cells (hMSC) that are grown on a TEM grid and differentiated into osteoblast cells (bone forming cells), we govern the deposition of pristine collagen fibrils. With this we aim to visualize – with unprecedented spatial / temporal resolution – both the structural development of the mineral phase and the associated interactions between the different organic, inorganic and cellular components that lead to collagen mineralization. Unraveling the details of this process requires the in situ microscopic analysis of the evolution of structure and morphology at nanometer resolution. For this we use both cryo TEM and liquid phase electron microscopy (LP-EM). Where cryo TEM allows the detailed analysis of structures in 3 dimensions, LP-EM allows the in situ imaging of processes in solution at video rate and with (sub-)nanometer resolution.

Project goals

The project will initially use the self-assembly of native collagen on TEM grids and in liquid cell chips to study collagen mineralization and organization.

This project is in a collaboration with Dr. Sandra Hofmann-Boss and Johanna Melke from the Department of Biomedical Engineering, TU/e.

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Introduction

Magnetite (Fe₃O₄) is a widespread magnetic iron oxide with many technological applications. Since its magnetic properties depend on shape and size of the crystals, crystal morphology control is important for application designing. Synthetic methods to form well-defined magnetite crystals use high temperatures and/or organic solvents. In contrast, aqueous synthesis at room temperature yields to poor control over size and shape. In nature magnetotactic bacteria can form well defined magnetite crystals with great control over nucleation and growth process. Biological systems can control nucleation and growth by combining the use of a poorly crystalline precursor phase and the interaction of minerals with biomolecular templates. We are focused on finding new bioinspired syntheses that combine the strategy known in nature to control the crystal size and morphology. To understand Fe₃O₄ formation mechanism we look at the early stages of nucleation and growth process and at the interaction of the inorganic/organic interphase. We combine synthetic design and full characterization of the materials with a wide-range of analysis techniques such as Raman spectroscopy, XPS, FT-IR, UV-vis, and (cryogenic) TEM.

Project goals

The goal of this project is not only to finding new bio-inspired syntheses that allow us better control over crystals features, but also to increase our understanding on the biomineralization process of magnetite. Gaining fundamental knowledge about how magnetite is formed can potentially allow the design of particles with tailored magnetic properties, which would pave the way for exciting new technological applications.
Introduction

Cobalt nanoparticles (Co NP) on support are used as the catalytically active phase to convert synthesis gas (CO, H₂) into long chain hydrocarbons. Preparation of the Co NP on catalyst supports is commonly performed by deposition precipitation (DP) method, of which the mechanism is not well understood. We will unravel the process of how Co precursor phase formed on support materials during DP reaction using cryoTEM and liquid phase TEM. This will be the first step for new improvements in optimizing the cobalt catalyst.

Project summary

Basically, the precursor phases are deposited on catalyst supports such as SiO₂ and TiO₂ (figure a), of which TiO₂ will end up with a higher activity and long chain selectivity catalyst. Our initial experiments on silica support show that the reaction starts with cobalt complex particles and ends with silica supported amorphous nanoplates (figure b). However the exact mechanism of deposition and the kinetics of the reaction are still not well studied. Those problems will be solved using CryoTEM, liquid phase (LP) TEM, liquid phase (LP) NMR, electron tomography and other advanced materials characterization method.

Project goals

1. CryoTEM, LP TEM and (LP) NNMR study on morphological, chemical and structural development of cobalt precursor phase on support.
2. Unravel the mechanism of the formation and crystallization of the precursor phase.

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2D-materials have gained significant attention over the past decades, due to their unusual properties. Synthesis of quasi-2D materials can only proceed via templating in a matrix. Here, we find inspiration from nature, where liquid crystalline arrangements of biomolecules are used to template the specific orientation of the inorganic crystals and where synthesis proceeds at RT in aqueous environments. Such materials which are common in nature (e.g. nacre, bone) have extraordinary properties like high mechanical strength etc..

Previously, it was shown that a porous smectic 6OBA/C6H liquid crystal (LC) system can template quasi-2D crystals of CaCO₃ from solution. First, the liquid crystalline state was polymerized, followed by a base treatment break the hydrogen bonding and open the pores. Then, the smectic structure was filled with CaCl₂, which was subsequently converted to CaCO₃. It was found the porous LC structure was filled with CaCO₃ layers with a thickness around 1.3 nm. This work provides a general pathway to designing ultrathin nanolayers in liquid crystalline systems.

In order to be able to rationally design complex hybrids, a fundamental understanding of the mineralization process is essential. This can be achieved by directly observing mineralization in situ with cryo-TEM and/or liquid-phase EM (LP-EM), which requires electron transparent TEM specimen that can be infiltrated by inorganic precursors.

Controlled deposition of LC based mineralization scaffolds with variable layer thickness and pore orientation in configurations that can be investigated by advanced TEM techniques such as CryoTEM or LP-EM. These will be used for time-resolved studies of infiltration and crystallization of inorganic precursors inside the LC template.
Bio Inspired Hybrid Actuators

Marina Pilz da Cunha

Introduction

Hybrid structures are found in diverse materials in nature, in which complex organization at the nanoscale between organic and inorganic components allows for advanced functional properties. For example, such hybrid nanostructures can be found in bone, seashells, lobster shells and teeth. The unique combination of organic and inorganic components in these materials allows for enhanced or novel properties and functions when compared to purely organic or inorganic materials. In this project, we concentrate on the development of bio-inspired hybrid actuators which are capable of responding to external stimuli such as light and air flow and generate electricity or act as soft robotics.

Project summary

In this project we are interested in the combination of flexibility offered by organic nanomaterials and the specific functionality and rigidity of inorganics, such as piezoelectricity. Additionally, by being a collaboration project between SMG and SFD, this project offers an unique opportunity and exposure to two complementary research fields, microscopy analysis and liquid crystal expertise.

Aiming at 2D metal oxide layers within a highly ordered nanoporous liquid crystalline film we will develop a new generation of hybrid actuators for applications including energy harvesting devices and soft robotic actuators.

Project goals

1. Design and prepare a layered liquid crystalline template with predefined nanometer sized pores
2. Successfully infiltrate the layered structure with minerals
3. Characterize the resulting structure through various methods including TEM and XRD
4. Analyze the piezoelectric abilities of the films and its response to external stimuli

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Understanding bio-inspired 2D crystal formation process

Yifei Xu

Introduction

Inspired by the mineralization process of bone, 2D crystals with thickness ~1 nm could be generated using charged polymers as nucleation inhibitor. Yet its formation mechanism is still not well understood. Our study in CaCO₃ model system have revealed that the process starts from amorphous calcium carbonate (ACC) clusters stabilized by polymers. In this project, the following formation process of 2D crystals will be investigated using Cryo-TEM, with a polymerized liquid crystal (LC) network as growth substrate. The knowledge will benefit a better understanding of biomineralization process and development of novel 2D crystal materials.

Project summary

The project focuses on understanding the bio-inspired 2D crystal formation process in CaCO₃ model system. To simulate the bone mineralization process, LC network membranes with ~1 nm lamellar nanopores will be used as the growth template, employing charged polymers (e.g., pAsp or DNA) as nucleation inhibitor. The formation process will be investigated in-situ using Cryo-TEM. Factors regulating the formation process such as supersaturation, pore thickness and polymer size will be explored to obtain a mechanistic insight. Based on the knowledge, the method will be extended for the synthesis of other 2D functional crystals such as ZnO or TiO₂.

Project goals

1. Understanding the formation process of 2D CaCO₃ crystal from ACC clusters
2. Extend the bio-inspired synthesis method to prepare 2D functional crystals

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Laboratory of Materials and Interfaces (SMG)
Bio-inspired synthesis of helical organic-inorganic hybrids

Mark van Rijt

Introduction

Organic-inorganic hybrid materials with helical arrangements are common in nature, exposing rather unique properties. For instance, the skin of the *Tmesisternus isabellae* beetle that turns red in presence of water or the *Stomatopod dactyl* lobster club which resists high-velocity impacts. To harness the potential of chiral hybrids as advanced materials for energy or coatings applications synthetic routes for their formation need to be established, especially extending the range of possible inorganic phases.

Project summary

Here we use a cholesteric liquid crystal (CLC) system exposing helical/chiral arrangement as templating matrix and attempt to mineralize it with inorganic phases such as calcium carbonate (CaCO$_3$) or zinc oxide (ZnO) (see Figure).

CaCO$_3$ is chosen to validate the experimental approach successfully applied to smectic systems and ZnO is of high technological interest in fields such as energy harvesting (piezoelectric properties), biomedical (biocompatible & antimicrobial properties) and luminescence (electro-luminescent properties).

By exploring a wide range of CLCs with varying pore chemistry a general approach for soft templating of minerals, metals or nanoparticles exposing an ordered helical arrangement may be found.

Project goals

1. Form defined chiral ZnO single crystals ideal for obtaining piezoelectric behavior, by using thin CLC as templated for ZnO biomineralization.
2. Determine the influence of the CLC pore structure and accessibility on the mineralization behavior.
3. Understand the mineral infiltration and ZnO formation inside the CLC structure by time resolved CryoTEM imaging.

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Introduction

Porous materials have many potential applications as insulators, sensors, catalysts and drug delivery vehicles, etc. Block copolymer amphiphiles can assemble into different morphologies such as spherical and cylindrical micelles or vesicles. In certain conditions they can also form nanoparticles with a bicontinuous internal structure. These bicontinuous polymeric nanospheres (BPNs) are promising candidates for the formation of porous silica particles by the sacrificial template method.

Project goals

1. Design principles for BPNs as building blocks with controllable diameter and pore structure
2. Obtain a library of silicified BPNs with controlled pore architecture
3. The formation of organized assemblies of silicified BPNs.
4. To obtain a fundamental understanding of the role of building block size, size distribution, and pore structure, on the mechanical and optical properties of the porous materials.

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Controlled pore architectures through co-assembly of silica and polymer based nanoparticles

Deniz Eren

Introduction

Colloidal self-assembly of organic/inorganic nanoparticles is a promising route for the formation of well-defined hybrid materials. A key challenge in this area is the synthesis the organic component with controlled size, surface charge and low dispersity. Here we employ amphiphilic block copolymers where alterations to the hydrophobic and hydrophilic blocks allow independent control over size and surface charge respectively. This allows us to control the assembly of silica nanoparticles and to investigate the effects of surface charge and size, on the assembly process and the final hybrid structure using CryoTEM.

Project goals

1. to obtain a better fundamental understanding behind the factors which govern the assembly of small building blocks into larger hierarchical structures.
2. to produce useful and affordable materials which have highly defined mechanical, chemical and structural properties for application areas such as; thermal insulation, catalyst fuel cells and oil spill remediation.

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Crystals are highly structured materials which can display interesting mechanical, optical, and chemical resistant properties depending on their polymorph. In this project we are investigating the self-assembly of organic/inorganic nanoparticles for the construction of well-defined hybrid colloidal crystals with tunable properties. Using silica and magnetite nanoparticles together with polymer latexes, we investigate the influence of the self-assembly pathway on the final hybrid structure using cryoTEM and liquid phase TEM.

**Project goals**

1. to understand the mechanisms behind the self-assembly of binary colloidal organic-inorganic systems, and use that mechanism to prepare hybrid materials that are ordered over multiple length scales.
2. to evaluate the thermal, optical, and mechanical properties of the materials and find the structure-function relationship.

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Organic photovoltaics (OPV) are being developed as an attractive alternative for inorganic solar cells due to their light weight, flexibility, processability and potentially low costs. However, OPV lack in efficiency and most notably stability to become established in the market. While a good understanding of the general design principles has been achieved (band gap, scale of phase separation, etc.), the local 3D interfacial structure and performance degradation due to defects or water and oxygen uptake have not been resolved.

To enable detailed interfacial characterization we employ model systems (Figure 1 a,b) that differ from a bulk heterojunction morphology (c). These model systems differ from the bulk heterojunction morphology to access the donor acceptor interface, since one can look directly along their interface. The model systems are prepared via either templating, from, e.g., phase separated polymer blends and lithography, or via the self assembly from soft spherical colloids. The process of model formation will be followed via (Cryo-)TEM, the 2D and 3D interfacial structure will be assessed via TEM and the chemical composition of the interface, dependent on processing, will be analyzed with EFTEM and EELS.

The goal will be the preparation of nanometer sized colloids suitable for OPV structures. This will be followed by the self-assembly of the colloids by spin-coating, drop casting, ultracentrifugation or other to create model systems including mono component or binary superlattices, compound colloids, etc. particular emphasis is placed on imaging the entire process of structure formation by in-situ electron microscopies (TEM, SEM) complemented by bulk analysis such as DLS and zeta potential measurements.

Laboratory of Materials and Interfaces (SMG)

3D interfacial structure and degradation of OPV

Zino Leijten

Introduction

Project summary

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Low Dose LP-EM for Multiscale Imaging

Hanglong Wu

Introduction

Liquid Phase Electron Microscopy (LP-EM) provides unique capabilities for probing the dynamics of nanomaterials in real-time, enabling the direct observation of structure formation over different length and timescales. However, regardless of the exciting success LP-EM has been achieved, it is still a relatively young technique with many limitations, among which electron-beam-induced artifacts is one of the most common, leading to misinterpretation of LP-EM data. Thus developing an imaging protocol with good resolution and minimized dose is highly desired.

Project summary

In this project, we aim to develop low-dose and contrast enhancement techniques relevant for LP-EM. We will use polymer, silica and hybrid nanoparticles with different sizes and electron scattering power, to evaluate resolution and contrast in low dose LP-EM. In addition, scripting will be used for beam manipulation and automated image acquisition. The developed protocols will be applied in multiscale imaging, more specifically, the self-assembly of block copolymers into bicontinuous nanospheres will be studied, as well as their subsequent mineralization with SiO₂.

![Figure 1](image)

**Figure 1.** Two examples of in-situ liquid phase imaging of block copolymer self-assembly via the solvent switch protocol.

Project goals

1. To optimize resolution and contrast for LP-EM of different materials and under different imaging conditions;
2. To establish low dose protocols for LP-EM of organic, inorganic and hybrid materials;
3. To monitor the development of hierarchical hybrid materials through the use of LP-EM;

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