Ion exchange, self-assembly, and light emission
A dance of ions and light
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Order in materials is the fundament of the world we live in. Without order, neither a cell nor a building would exist. Biological materials are ordered with unprecedented complexity across length scales to achieve extraordinary performance. Human-made materials alike perform best when made from hierarchically ordered building blocks. Such ordered materials often consist of two or more components that together form a composite material which can exhibit material properties beyond the ones of their individual components. The order in composite materials can reach down to the nanoscale, thereby creating extraordinary material performance that surpasses the performance of the individual bulk materials. A simple, yet impressive example is the hardness of nacre in seashells. Long before humans had the means to probe the nanoscale, they already had developed processes that exploit order at that scale, for example, by encapsulating fragile pigments in nanoscopic host matrices to create paintings withstanding UV irradiation and heat. When materials science flourished in the 20th century, researchers started to deliberately compose materials of intricate complexity across various scales, ranging from fiber-reinforced polymers to integrated electronic circuits. While humans achieve increasingly complex architectures, the processes are oftentimes difficult and cumbersome, leaving nature’s extraordinary structuring capabilities unmatched. Therefore, developing new, nature-inspired, design routes of fabrication will allow to gain control over multiple material properties with increased performance while facilitating the fabrication process.

1.1 Self-Assembly

Humanity has always shaped its surroundings, and its ability to do so is mostly defined by the available tools. While fabrication techniques have evolved in precision to create fine mechanics in a watch and nanometer-sized features in integrated circuits, those approaches require sophisticated processes. Often, the material is machined from the bulk down to the desired shape and composition, giving it the name ‘top-down’ manufacturing. The laboriousness of ordering material at such small scales sparks the desire to find different routes starting from the ‘bottom-up’ where material forms itself (once the right conditions are met). For nanoparticles, this implies to assemble them from molecular precursors, which is intuitively advantageous over milling down bulk material.
Nanoparticles give access to another bottom-up route for building materials. Intricate architectures can be assembled from distinct building blocks by exploiting their material specific interactions. Tailoring these interactions allows to direct how building blocks arrange into an ensemble, thus giving it the name directed-assembly or self-assembly: “Self-assembly is the autonomous organization of components into patterns” - G. M. Whitesides. This is one of the few available processes to order materials at the micro- and nanoscale. Self-assembly exhibits many desirable properties: the processes often take place at moderate reaction conditions, are very easy to scale and don’t require sophisticated cleanroom facilities.

### 1.1.1 Ordering in Natural Materials

In living organisms, matter is organized at all scales. This phenomenon is so profound that, even on the smallest scale, the complexity of a molecule can serve as an indicator whether an organism had formed it. On a slightly larger scale, organisms embed micro- and nanometer sized crystals into amorphous matrices to synthesize architectures beyond crystallographic symmetries.

![Figure 1.1: Order in natural materials. a) Skeleton of a sand dollar. b) Pavilion constructed following the light-weight design principles of the sand dollar skeleton. c) Brittle star, a sea star whose skeleton is covered with d) calcium carbonate micro lenses, allowing it to “see” e) Abalone shell with iridescent nacre. f) SEM micrograph of fractured nacre revealing the layered architecture.](image)

This so-called biomineralization with its hierarchical organization of composition allows creating architectures with orthogonal properties (e.g., light and tough) for considerably different purposes, oftentimes even from the same material. The diversity in functionality that can be achieved through arranging the same

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material in different ways becomes especially evident when studying calcium carbonate biominerals: the double-curved shell of sand dollars has served as blueprint for lightweight and strong buildings,20 the nacre of an abalone shell protects the organism and fascinates humans with its iridescence,4,21 while the accurate crystallographic alignment of calcite allows the brittle star to “see” with its skeleton (Figure 1.1).16 That all these functionalities are based on the same mineral illustrates a general theme in biomineralization—a limited selection of crystalline materials is combined with amorphous matter to yield architectures with different functionalities. It is thus through the order within a material that functionality can be designed to tailor individual properties separately and outperform bulk properties by far. Hence, taking inspiration from biominerals to develop simple routes to synthetic, hierarchically ordered structures offers great opportunities for new ways to fabricate functional materials.

1.1.2 Synthetic Self-Assembly

Humans possess an innate admiration for the patterns found in nature.18,22,23 Fascinated by the seemingly effortless manner with which those processes take place, scientists took inspiration and developed self-assembly systems to create architectures from the bottom up.2,3,7,8,10,24–32 Despite tremendous progress, synthetic self-assembly approaches are yet to meet the grace and complexity found in nature. However, while nature is limited to a small set of compounds,13 synthetic approaches can choose from a wide variety of materials, thus allowing to create architectures for applications such as optics, (opto-)electronic and catalysis.10

The potential of tapping into this vast variety of synthetic materials is exemplified by colloidal self-assembly.8,9,11,26,33–38 This approach thrives through its simplicity—it is the assembly of structures from particles in solution and thereby gives accesses to the tremendous variety of nanoparticles synthesized to date.8,39

By exploiting physical and chemical interactions of those nanoparticles in solution, architectures harnessing the versatility of their building blocks have been assembled, serving fields such as optics, magnetics, catalysis, and electronics.8 Furthermore, new properties can even emerge from the ordering itself rather than the material properties alone. A visually appealing example are synthetic opals (photonic crystals) that use order on the scale of the wavelength of light (Figure 1.2).40,41 The sequence in which the building blocks assemble is programmed by the interaction of the particles with each other. Mainly, they can attract or repulse each other in many specific manners. Careful tuning of these interactions allows controlling the final design, e.g., through tailored surface morphology and chemistry (Figure 1.2c, d).8,9,33 Even more complex architectures can be obtained by introducing multiple particle species to the self-assembly process, or through coprecipitation with amorphous material.42,43
Exploiting particle interactions to create architectures makes self-assembly approaches scalable and straightforward. However, due to the ordered packing between the individual particles, the results are dominated by symmetric superstructures. Overcoming these restrictions and introducing in-situ control over the assembled morphology will be essential for a more widespread application of bottom-up assembly.

**Figure 1.2:** Synthetic self-assembly. a) Ordered monolayer of silica colloids giving rise to b) structural color under white light.\(^4\) c) Anisotropic polymer colloids.\(^9\) d) Triblock Janus particles with hydrophobic poles assembling into a Kagome lattice.\(^4\) e, f) Hierarchically ordered photonic ball based on polystyrene colloids, SEM and optical micrograph.\(^4\) Copyright note: \(^2\)

### 1.2 Self-Assembled Carbonate Microarchitectures

Spontaneous pattern formation processes can yield complex arrangements that are not restricted to repetitive lattices.\(^1\) Sometimes, when the interplay between two components is defined by diffusion and reactions, complicated patterns emerge that can be controlled through the modulation of the reaction conditions.\(^1\) Intricate 3D architectures can form during the reaction/diffusion controlled self-assembly of carbonate microarchitectures (Figure 1.3).\(^2,29,46-53\)

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1.2. SELF-ASSEMBLED CARBONATE MICROARCHITECTURES

Figure 1.3: Typical self-assembled carbonate architectures. a) Coral-like shapes (left to right: typical corals, top-view of a field of corals, coral overgrown with vases). b) Stems (left to right: row of stems, top-view onto stems, typical coral overgrown with stems, small coral overgrown with stems). c) Vase-like shapes (left to right: typical vase, vases and stems on rough aluminum, stem transitioning into a vase with thick rim, very small vase). d) Leaf-like shapes (left to right: leaf with upright helix, leaf overgrown with stems, leaf with horizontal helix, leaf with double rim). e) Helices (left to right: double helix, cross-section of double helix revealing the internal layout, double and single helix, double helix in comparison to a simulated one\(^{49}\)). *Simulation in e) adapted with permission.*\(^{49}\) *Copyright 2017, AAAS.*
These hierarchical composites of almost life-like appearance can be grown from solution and are composed of earth alkali metal carbonates (BaCO$_3$, SrCO$_3$, and CaCO$_3$) and silica. First discovered by García-Ruiz, they are often referred to as “Biomorphs” for their striking resemblance to biogenic minerals, albeit the absence of organic molecules during the synthesis. Soon, shapes where synthesized that do not have a natural look-alike. In this work, we therefore refer to them as (micro)architectures. The synthesis of these architectures offers a broad variety of shapes (corals, vases, stems, helices, and others) with morphology control through external parameters (Figure 1.3).

1.2.1 Synthesis of Carbonate Microarchitectures

The complexity that can emerge from such simple starting materials as barium ions and metasilicate has intrigued many researchers to study their formation in great detail. These studies have led to a better understanding of the system itself, as well as given the means to control and even model their growth. The microarchitectures can be described as an ordered ensemble of elongated nanocrystals ($\approx 20$ nm) that together form the microscopic shape (10-100 µm) and follow the curvature of the microarchitecture. The nanocrystals are embedded inside a silica matrix. The microarchitectures are formed in aqueous solution (or gels) from earth alkali metal ions and silica under CO$_2$ influx. Conventional colloidal self-assembly approaches are a sequential process, first nanoparticles are synthesized, then they are assembled. In contrast, carbonate microarchitectures are synthesized in a single process. Here, the nanocrystals form from solution at the growth front to assemble into the microarchitecture - resulting in a single-step, fast, and straightforward fabrication.

The system is based on coprecipitation of earth alkali metal carbonates (BaCO$_3$, SrCO$_3$, and CaCO$_3$) and polymerization of silica, which are linked through an acid-catalyzed feedback loop. In the case of barium carbonate, CO$_2$ from the atmosphere diffuses into the solution and triggers BaCO$_3$ precipitation. Strontium and calcium follow an almost identical mechanism. This can be described by the following simplified reaction:

$$Ba^{2+} + CO_2 + H_2O \rightarrow BaCO_3 + 2H^+. \quad (1.1)$$

If the bulk solution is more alkaline than the regime of silica polymerization, the formation of H$^+$ locally decreases the pH at the growth front until the pH for silica polymerization is reached. The simplified reaction can be written as:

$$SiO_2^{2-} + 2H^+ \rightarrow SiO_2 + H_2O. \quad (1.2)$$

The local decrease of pH at the growth front causes the silica to polymerize on the crystallizing BaCO$_3$, thereby blocking its growth and restricting the crystals to nanometer sizes. The constant influx of CO$_2$ drives the formation of new BaCO$_3$
crystals, which again will be encapsulated by silica. This so-called coprecipitation results in an ensemble of nanoscopic crystals that are individually sealed by a thin layer of silica, and as a whole covered by a thicker layer of silica. The polymerization of silica is pH-dependent and has a narrow optimum. Growth can take place on either side of this optimum (Figure 1.4). In both cases, the process starts with BaCO$_3$ nucleation. On the far alkaline side of the silica optimum, the local pH decreases until the regime of silica polymerization is met. Then, growth is favorable towards the bulk of the solution where the pH is more alkaline, growth in that direction is therefore not inhibited. The resulting carbonate microarchitectures resemble stem-, vase-, or coral-like shapes (Figure 1.4, region 3). Starting much closer to the silica optimum, BaCO$_3$ nucleation decreases the pH below the optimum for silica polymerization. Here, growth towards the bulk of the solution results in reaching the silica polymerization optimum and blocking of growth. Therefore, structures grow towards each other or flat on the substrate, resulting in coral or leaf-like architectures. (Figure 1.4, region 2). Starting the reaction at a pH below the silica polymerization regime results in the growth of conventional whitherite crystals, as no silica can polymerize (Figure 1.4, region 1). This oscillating interaction continues until the consumption of precursors and the influx of CO$_2$ have disturbed the balance of the coprecipitation.

![Figure 1.4](image)

**Figure 1.4:** Schematic of barium carbonate/silica coprecipitation. Adapted with permission of W. L. Noorduin. Left: schematic of the pH dependence. Right: resulting shapes. Silica polymerization is optimal within a narrow pH regime ($pH_{SiO_2}$). Starting with a bulk pH in regime 3, BaCO$_3$ nucleates and thereafter its growth decreases the local pH at the growth front until the pH-regime of silica polymerization is met. Then, silica formation inhibits the growth. The bulk pH remains higher, which allows the growth to continue towards the solution creating architectures as seen on the right side, region 3, as well as in Figure 1.3a–c. In regime 2, the drop in pH, caused by the BaCO$_3$ formation, moves the growth front onto the left side of the silica optimum. Here, the growth direction is opposite, growth towards the bulk solution results in reaching the silica polymerization regime, thus blocking the growth. Architectures, therefore, grow towards each other, as seen in region 2 on the right side and in Figure 1.3d–e. Growth of BaCO$_3$ in regime 1 does not trigger silica precipitation; therefore, only conventional whitherite crystals form.
As this system is based on the interplay of different reactions, it is possible to direct the growth by changing the balance between them. The main handles to steer the growth can be derived from the dependencies apparent in the reaction scheme. Modulation of the CO$_2$ influx can be used to increase the BaCO$_3$ precipitation, which can yield vase-like shapes. Adjustment of the pH does not only enable to enter two distinctly different growth regimes but also to allow tuning the growth within these regimes. The temperature-dependent solubilities and reaction rates offer yet another way to manipulate growth. Collectively these insights have led to the development of models that can reproduce the growth of known structures and can predict new ones (Figure 1.3e). Beyond these intrinsic parameters, crystal growth is very susceptible to the incorporation of additives that may allow extreme alterations of the morphology.

### 1.2.2 Prospects of Carbonate Microarchitectures

A unique characteristic of the metal carbonate/silica coprecipitation system is the hierarchy in its architecture. The interplay between carbonate and silica results in short-range ordered nanocrystals (typical size 10-30nm) which are enveloped by thin layers of silica. On the micrometer scale, long-range order between the crystal ensemble and the morphology emerges as they follow the local curvature. Furthermore, the crystals align their elongated shape (they are elongated along their crystallographic c-axis), while the silica passivation of the crystal growth ensures a quasi-monodisperse crystal size distribution.

In colloidal assembly approaches, the particles are typically synthesized and functionalized in a separate step before the assembly. The prior functionalization encodes the final structure already into the individual particles and thereby limits the possibilities to steer the assembly process dynamically during assembly. In contrast, the growth of carbonate microarchitectures is based on coupled chemical reactions that are sensitive to external stimuli that shift the balance in their interplay. Hence, the shape of the architecture can be manipulated during the growth process. This dynamic steering allows constructing architectures one step closer to the finesse found in nature.

While colloidal assembly accesses many materials but is very limited in the accessible shapes, these carbonate architectures offer many shapes but are restricted to a few carbonate salts (BaCO$_3$, SrCO$_3$, and CaCO$_3$) in combination with silica. This limited choice of materials may partially be compensated by post synthesis functionalization of the outer silica layer, yet widespread technological applications will require the accessibility of different material compositions.
1.3 Self-Assembled Crystals and Light

Crystals have always fascinated humans with their shine.\textsuperscript{21} Therefore, crystals have been a topic of interest for many scientists that explored their ability to manipulate light, at least since Vikings used birefringent to navigate (Figure 1.5e).\textsuperscript{57,58} The discovery which sparked plenty of research in the interactions between light and crystals was Arago’s observation in 1811 that linear polarized light undergoes a rotation when transmitted through quartz.\textsuperscript{59} This insight was followed by many experiments that contributed to the understanding of how light interacts with chiral media.\textsuperscript{60–63} Scientists discovered that crystals also could be chiral, and depending on their handedness, will rotate light to the left or right.\textsuperscript{63} In α-quarz, for example, the order of the atoms in the crystal lattice is chiral. This chirality can be mimicked through a twisted stack of linearly birefringent sheets of mica.\textsuperscript{64,65} In these so-called Reusch piles, named after the scientist who discovered them, the chiral behavior is absent in the individual sheets and emerges from their order. While the order of a crystal structure is difficult to change, the alignment of mica sheets can easily be modified. A modern-day implementation where light follows the twist of a crystal can be found in liquid crystal displays. These liquid crystals can undergo a phase transition from linear (nematic) to chiral (cholesteric) and thereby rotate light, which is used to switch pixels on and off. This demonstrates the ability of ordered crystalline ensembles to manipulate light. Gaining control over assembly of those ensembles is a powerful tool that will allow to design the response of light to a material.

Nature has developed many ways to manipulate light by creating sophisticated order of materials (Figure 1.1c-f and 1.5a-c).\textsuperscript{66–69} An example that highly resembles modern-day optical fibers is the silica skeleton of a marine glass sponge (Figure 1.5c).\textsuperscript{70} Other organisms have also shown excellent control over crystal growth; a prime example are the calcite eyes of brittle stars (a type of sea star) (Figure 1.1c, d).\textsuperscript{16} Here the shape is optimized to focus light on the underlying neural cells, and even the crystallographic orientation is optimized to minimize optical distortion. There are many more examples of natural optical structures,\textsuperscript{69} all of which are formed under ambient conditions and mild temperatures. These moderate reaction conditions in nature stand in sharp contrast to the oftentimes harsh conditions and elevated temperatures of industrial manufacturing.

Aware of the potential that lies in the ordering of matter and fascinated by the finesse of natural systems, scientists used self-assembly to create materials with optical functionality (Figure 1.2).\textsuperscript{19,32} The many examples span a broad spectrum: some are mimicking their biological counterparts (Figure 1.5d),\textsuperscript{25} others create advanced optical components such as glass fibers with integrated sensors,\textsuperscript{71} or exploit periodicity to create structural colors (Figure 1.2).\textsuperscript{40,72–75} Overall, the assembly from small units creates materials that cannot exist in bulk and that have material properties that emerge from the composition and order in the assembly. We en-
vision that the development of strategies that offer control over the alignment of individual building blocks, as well as control over the microscopic morphology will result in materials with novel functionalities.

**Figure 1.5:** Optical structures. a) Photograph of Morpho butterfly wing and b) SEM micrograph of the color-giving ordered structure. The layered architecture resembles commercial optical fibers used for telecommunications. c) Spicule of a silica-based sea sponge, the layered architecture resembles commercial optical fibers used for telecommunications. d) Self-assembled calcium carbonate microlens array projecting the letter “A”. The architecture is mimicking the eyes of the brittle star (Figure 1.1c, d). e) Calcite crystal, which due to its birefringence, splits an unpolarized laser beam into two polarized beams. Vikings likely used this to navigate on cloudy days.

1.4 Controlling Chemical Composition Using Ion Exchange

Self-assembly has brought sophisticated spatial control over materials by arranging them from single building blocks into functional structures. Mostly, the building blocks are nanoparticles. These nanoparticles exhibit a wide variety in their size, morphology, composition, crystallinity, and surface functionality, which define their specific electronic, optical, magnetic, or catalytic activity. Ideally, those properties would be controlled independently. However, the properties are entangled by their synthesis route. Consequently, not all properties of nanoparticles can be controlled independently, making some combinations inaccessible.

The chemical composition can, for ionic nanoparticles, be manipulated post-synthesis through ion exchange reactions. This approach starts with the

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synthesis of a particle which differs in composition from the desired one but matches the targeted properties such as shape and crystal structure. Post synthesis, the material is then converted to the desired composition through an ion exchange reaction. In this process, one ionic species is replaced by another one of similar size and commonly also identical charge.

Ion exchange reactions have a long history: they are known to occur in rocks and fossils and have found technological application in thin films to create waveguides or modify semiconductors. Applying these types of reactions to nanoparticles has sparked a new field that developed new ways to control the chemical composition of particles. Remarkably, ion exchange retains some properties of the original crystal such as crystal-lattice and morphology, while changing the material composition of particles entirely or selectively. Thereby, ion exchange offers an opportunity to disentangle shape and chemical composition, and provides new ways to expand the already extensive library of nanoparticles by compositions that formerly were inaccessible.

The last two decades have brought significant advances in the understanding of the underlying principles of ion exchange reactions. A fundamental requirement is the possibility for one ionic species to leave the crystal and the availability of another ion to take its place (Figure 1.6a–c). The supply and removal of ions are often mediated by solutions and sometimes also by gas phases. Intuitively the process can be understood as a striving for equilibrium (following Le Chatelier’s principle). An ionic crystal AX constituted of A\(^+\) and X\(^-\) can potentially undergo an ion exchange to BX when exposed to an abundance of B\(^+\) ions. Therefore, AX has to undergo dissociation, A\(^+\) solvation, B\(^+\) desolvation, and BX association. The energies associated with these processes determine whether or not the ion exchange is thermodynamically feasible. The association and dissociation energies largely depend on the lattice energy of the ionic crystal, while (de-)solvation is driven by the affinity of the ions for the solvent and the solubility constants.

Besides the thermodynamic considerations, it is essential to understand the practical implications that arise from the kinetics. In order to replace one ion by another, ions have to move through the solution towards and away from the crystals. The rate of the reaction is mostly determined by the surface to volume ratio of the crystals and the diffusivity of the individual ions. More importantly, ions also need to move inside the crystal. Their transport is commonly supported by vacancy or interstitial diffusion (Figure 1.6a–c). These diffusion processes inside the crystal depend on many factors, one of them being the size of the ions that are exchanged, as larger ions generally diffuse slower. Furthermore, the ability of a crystal to accommodate strain, which is much higher in nanocrystals than in bulk, assists the movement of ions. Overall, cation exchange in nanocrystals has been widely studied. Exchanging anions remains difficult, primarily because of their larger size and thereby slower diffusion rates. Ion exchange in bigger,
microscopic, architectures is more challenging than in nanoparticles due the much longer diffusion paths that often prevent a complete exchange.

FIGURE 1.6: Ion exchange reactions. a–c) Simplified schematic depicting the ion exchange from ZnSe to CdSe via interstitials and vacancies, following the mechanism proposed by Groeneveld et. al.⁸⁹ b) Sequential ion exchange of a copper sulfide nanorod into a multiphase particle.⁸⁴ Copyright note:⁴

Based on these insights, many ion exchange reactions have been developed, thus expanding the already vast library of nanocrystals synthesized to date. Apart from complete conversion, partial conversion also allows to create alloys and spatially organize separate phases (i.e., core-shell) of an otherwise inaccessible complexity (Figure 1.6d).⁸³–⁸⁵ First steps beyond the conversion of individual particles have been explored by converting nanoparticle films in combination with lithographic techniques to create patterns (Figure 1.7d).³⁴,⁸⁵,⁹⁵,⁹⁶ In order to unleash the potential of ion exchange, there are two main challenges to overcome. First, the size limitations, which mostly arise from diffusion, make ion exchange impractical for microscopic and larger structures. Here the role of the anion is especially important as its larger size hampers diffusion. Second, ion exchange reactions are typically applied on the entire sample. Gaining spatial control over ion exchange reactions may also pave the way for alternatives to current lithographic approaches. Eventually, these advances could enable a seamless integration of ion exchange and self-assembly techniques, ultimately obtaining independent control over the shape and composition of materials.

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1.5 Perovskites

The rise of semiconductors has set the foundation for the digital age. Over time, the semiconductor industry continuously innovates to create smaller integrated circuits with increasing complexity and solar cells of higher efficiency. The continuously increasing performance comes at the cost of requiring advanced, costly clean room facilities, thus limiting the accessibility of this research. A material class that has made semiconductor research, especially solar cell research, accessible to a broad group of scientists by requiring only minimal technological prerequisites are lead halide perovskite semiconductors. Within a decade of being first implemented in a solar cell, efficiencies almost match those of silicon-based cells which have been researched for 60 years.

While the term perovskite is often used synonymous for semiconducting lead halide perovskites, it refers to an ionic crystal structure \( \text{ABX}_3 \) in which \( A^+ \) and \( B^{2+} \) are cations of fundamentally different sizes, and \( X^- \) the anion (Figure 1.7a). This crystal structure was first recorded as mineral in 1839 (calcium titanium oxide). Remarkably, it is only since 2009 that this perovskite crystal structure got widespread attention due to the first implementation of methylammonium lead halides in a solar cell. One of the most popular examples is MAPbBr\(_3\) with methylammonium, lead, and bromide, respectively. Other common cations are formamidinium and cesium, while the halides are typically chloride, bromide, and iodide as well as mixtures thereof. Unlike covalently bound semiconductors, their ionic nature allows for simple solution processing. Choices in the halide moiety enable straightforward adjustments in composition to tune the bandgap. It might be this ease in fabrication in combination with their excellent optoelectronic properties and tolerance to defects that have resulted in the manifold applications including devices such as LEDs, detectors and scintillators (Figure 1.7). While solar cells only require continuous layers, these integrated devices also demand lateral patterning of complementary materials such as insulators and semiconductors of different bandgaps. Already a remarkable level of patterning control has been achieved, such as local tuning of the bandgap through ion exchange. Moreover, spatial positioning of material has been achieved by techniques such as lithography, laser writing, inkjet printing, templates, and self-assembly of nanoparticles. Overall, this highlights the potential for patterning perovskites in two dimensions as well as developing routes to sculpt perovskites in three dimensions.
CHAPTER 1. INTRODUCTION

FIGURE 1.7: Lead halide perovskite semiconductors. a) Cubic perovskite crystal structure showing a methylammonium or formamidinium anion surrounded by four PbX$_6$ octahedra. b) CsPbX$_3$ mixed halide nano crystals under UV light, exhibiting fluorescence at different wavelengths depending on their composition. c) CsPbX$_3$ perovskite emitting light under X-ray radiation, demonstrating the applicability in scintillators (detection of X-rays by conversion of X-rays into visible light, detectable by a conventional CCD). d) Photoluminescence micrograph of CsPbBr$_3$ nanocrystalline film which was locally ion-exchanged to CsPbI$_3$, using X-ray lithography. e) Methylammonium lead bromide-iodide LED. f) Flexible perovskite solar cell.

1.6 Motivation and Outline

Self-assembly and ion exchange are two versatile concepts for the creation of complex architectures and control over the composition of materials. In this thesis, we pose three questions regarding the application of these concepts. First, how can we manipulate light with self-assembled BaCO$_3$/SiO$_2$ microarchitectures? Second, how can we use ion exchange reactions to replace the material inside these microarchitectures for a semiconductor? And third, what does it take to ‘print’ ion exchange reactions onto a material to control the composition of a material locally? This thesis addresses these questions experimentally through optical studies of self-assembled helices, ion exchange on microarchitectures, and patterned ion exchange reactions in thin films.

In chapter 2, we study the potential of self-assembled carbonate double helices to manipulate light. We incorporate fluorescent molecules into the structure and show that light emitted from these molecules is wave-guided and leaves the helix at the tip in a narrow beam. The helix thus acts as a directional emitter. Furthermore, light transmitted through the helix experiences circular retardance specific
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to the handedness of the helix. We attribute this behavior to the chiral ordering of the birefringent barium carbonate nanocrystals within the helix. Collectively, these observations demonstrate the ability of self-assembly to hierarchically order matter into materials with emerging functionality.

In chapter 3, we present an approach to expand the BaCO$_3$/SiO$_2$ coprecipitation system to different materials by post-synthesis shape-preserving conversion reactions. We develop an ion exchange route that first replaces the barium for lead and then the carbonate for methylammonium halide, creating methylammonium lead halide, a semiconductor with outstanding optoelectronic performance. While ion exchange reactions are often developed for individual nanoparticles, the hierarchical nanocomposite layout of these architectures allowed us to exchange the material fully with retention of the intricate morphological features. We show that this approach can be transferred to other nanocomposites by applying it to the conversion of biominerals.

In chapter 4, we introduce the concept of ion exchange lithography (IEL). Based on the ion exchange reactions developed in chapter 3, we use methylammonium and formamidinium halides in solution as reactive “ink” and lead carbonate nanoparticle films as ion exchangeable “canvas”. By spraying, stamping and painting the ink on the canvas we demonstrate controlled patterning of electrically insulating films and semiconductors with tunable optoelectronic properties. Moreover, we show that the IEL approach can be integrated into the fabrication of (opto)electronic devices such as light-emitting diodes (LED).

Overall, this thesis shows the potential of hierarchical self-assembly strategies to create ordered ensembles with emerging functionality. We explore their ability to manipulate light, as well as their advantages in ion exchange processes given by their architecture. With this, we decouple shape and composition in self-assembly of metal carbonates, expanding the material repertoire to state-of-the-art semiconductors. Finally, we develop a lithography method based on ion exchange reactions to create patterns that may open up new routes for the fabrication of integrated devices.