On the conversion of nanocomposite architectures

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Chapter 1

Introduction
1. Introduction

1.1 Progress in Man-Made Materials

"...remember that a CPU is literally a rock that we tricked into thinking”
Ben Driscoll

In this world there are many compounds with fascinating properties. Just as silicon can be 'tricked' to become a powerful computer, so too can we trick cobalt to become a versatile catalyst or lead to be a tunable semi-conductor.\textsuperscript{1–3} In fact, one could consider that tricking elements into doing what we want has played a pivotal role in the development of our society.\textsuperscript{4} From the very early days of using stone, bronze and iron to create tools, to the industrial revolution using coal to power our factories, utilizing the power a compound possesses is crucial to our technological progress.\textsuperscript{5,6}

The utilisation of such a compound is linked to how well we can give it a proper shape: An axe is dysfunctional without a sharp edge, just like a battery will not power anything if it short circuits. It is the combination of composition and organisation that makes a compound a functional material. In our thousands of years of material-making, we have developed many ways to shape materials either in large numbers or in specific morphologies.\textsuperscript{7,8} However, our ability to do so depends on the scale of the particular material. Shaping a material not only becomes more difficult when it becomes too large to handle, but also when it becomes too small to manipulate easily.\textsuperscript{9} In fact, a big challenge in our current age is to gain control over a material on the nano- to micrometer scale.

Though the nano- to microscale is invisible to the human eye, the effects of the organization at this scale are very visible. For example, solar cells rely on their organisation at this scale to obtain high conversion efficiencies, while catalysts work best as tiny nanoparticles embedded on a supporting material (Figure 1.1).\textsuperscript{10,11} Thus, organization on this invisible scale gives access to sources of renewable energy and ways to create various compounds. Yet, organizing at this scale is not trivial, and often requires elaborate setups to properly shape the correct compounds.\textsuperscript{12,13}

![Figure 1.1: Examples of man-made materials whose functionality is derived from order at the nano- to micrometer scale.](image)

Solar cells (left) are commonly composed of nano/micrometer-thick layers to convert a high fraction of incident light directly into usable current. A catalyst (right) on the other hand often has the shape of a metallic nanoparticle (in green), which lowers the energy barrier of a chemical reaction. © by Fabian Ruf / Scilight (left) and ICMS Animation Studio, TU/e (right).\textsuperscript{14–16}
There is an ongoing research effort to facilitate the organization of a material for a specific purpose by tuning either its shape or composition. Take for example solar cells, which in the commercial world are mostly silicon-based. Even though silicon is one of the cheapest elements on earth, the production costs of a silicon-based solar cell are still relatively high. This is because the silicon is organized as a single crystal when incorporated into a solar cell, which is done by carefully stacking it from the molecular level up.\(^{10}\) Currently, a new solar cell material, perovskite, has therefore attracted much attention in the scientific community as it does not require this single crystal organisation. These perovskites thus require significantly less effort put into their organization to be functional and therefore are interesting additions or even proper competitors to silicon-based solar cells.\(^{3,17}\) Hence, replacing silicon with perovskite as the composition of a solar cell may reduce the need of organization of a solar cell, while still maintaining its functionality.

This does not abolish the function of organization however, as it can also improve the performance of an already active compound. In catalysis oftentimes metal particles such as iron, nickel or cobalt are used to catalyze a myriad of processes.\(^{18–20}\) Though these metals are active on their own, their performance is increased when embedded as nanoparticles on a supporting material like SiO\(_2\), Al\(_2\)O\(_3\) or TiO\(_2\).\(^{21–23}\) Moreover, by tuning organizational parameters like spacing, particle size and surface area, these supported catalysts can be tuned to increase their activity or produce specific products.\(^{24–30}\) In other words, the performance of a catalyst can thus be enhanced by designing an effective organization of its active components.

Supported catalysts are also an example of functional materials formed using multiple compounds as building blocks. The functionality here can be derived from the individual building blocks, or from an interplay between them. One class of materials that demonstrate this very well are nanocomposites, materials where nanosized building blocks are incorporated into a carrier compound.\(^{31}\) Functionality can be introduced along multiple length scales with this structural layout, for example by spacing the nanoparticles with a fixed distance.\(^{32}\) This systematic structuring introduces new properties not found in an individual nanoparticle or their bulk counterpart, creating interesting opportunities for optical, electromagnetic or mechanical purposes.\(^{33–36}\) The possibilities for these nanocomposites are increasing with each new building block found, for example with novel particle syntheses that create new compound-, size- and shape-selections.\(^{37}\) Combine this with an ever-increasing list of assembly techniques, and the potential for properties programmed into nanocomposites is still yet to be fully realized.\(^{38}\)

Despite tremendous progress in this field already, the current available methods are not yet all encompassing and oftentimes require elaborate setups to shape their building blocks. These methods can generally be divided into two approaches: top-down and bottom-up.\(^{31}\) With the top-down approach, materials are shaped from the macroscale down using for example 3D printing, which is limited to printable materials and is not easily scalable.\(^{39}\) The bottom-up approach on the other hand is based on assembly from the molecular level up. Unfortunately, it requires pre-existing templates to guide the material in the proper shape. These templates need to be made in a cleanroom and have limited out-of-plane options.\(^{40}\) There are some solutions that circumvent these problems, for instance using silk worms’ fibroin to outsource the (mass-)production of a 3D template to nature.\(^{41}\) This however limits the choice of shapes to those pre-fabricated by nature. Perhaps if we could understand the mechanisms used by nature to fabricate materials, we could utilise them to make our own, freely shapeable, materials.
1.2 Lessons from Nature

On the full timeline of our planet, mankind’s conscious efforts to produce materials is a relatively new process. Organisms found in nature (i.e. animals, plants and even our own human bodies) have had a significantly longer time to develop materials required for their survival and procreation. This has resulted in a myriad of materials with widely varied properties e.g. tough shells, colorful butterfly-wings, sharp teeth, durable spider silk and rigid bones among many other examples (Figure 1.2). What makes the production of these varied materials even more remarkable, is that the organisms who made them only used a relatively small selection of compositions, mostly composed of polysaccharides, proteins, and minerals.

Oftentimes various organisms even use the same building block to create very different materials. For example, α-keratin is used by both porcupines and sheep. The former makes spiky quills out of it to protect itself from predators, while the latter makes warm wool to help regulate temperature. So how can the same building block yield materials with such different properties? The answer to this lays in the ordering of this material. The keratin in the porcupine’s quills is organized in a stiff outer sheath and a porous core, resulting in a strong, yet lightweight, defense mechanism. Sheep’s wool also consists predominately out of keratinous proteins, but these are organized into a matrix with helical shaped cells at its core. Now, a material with mechanical and thermal properties is produced, beneficial to both the sheep and the textile industry. The effort nature puts in the organization of its materials thus results in specific properties derived from this organization.

Figure 1.2: Examples of materials produced by nature. Even though these materials have widely varying mechanical properties and applications, they are predominantly composed of just polysaccharides, proteins and minerals. Reprinted with permission from Eder et al., Science 2018.
Other fascinating examples of the care nature puts in organizing materials can be found in processes where living organisms produce minerals. These biomineralization processes revolve for the most part around four classes of minerals: calcium carbonate, calcium phosphate, silica and magnetite. Here, the shape of these minerals is vital for their performance inside the organism. For example, magnetotactic bacteria use the magnetic field lines of our planet to orient themselves. They do so with special organelles called magnetosomes, in which magnetite is the magnetic component. In order to shape the magnetite to fit the organelle, the bacteria employs a special protein which single-handedly shapes the magnetite in 20-30 nm superparamagnetic crystals, making it suited for its directing purpose.

The organization in biomineralization is also apparent in the most common of biominerals: calcium carbonate (CaCO$_3$). Its crystal structure is quite shapeable, as it exists in three crystalline polymorphs: calcite, aragonite and vaterite. In addition to these crystalline polymorphs, it also exists in a few amorphous states. Especially amorphous CaCO$_3$ (ACC) is vital in nature, as it acts as a precursor which can be molded and crystallized to the crystalline polymorphs of CaCO$_3$. Using an amorphous intermediate instead of direct crystallization allows sculpting of the overall crystal shape at the same time. For example, sea urchins shape their spines by crystallizing ACC into calcite. By doing so, they are able to create a single crystal of calcite in a smooth spine-shape, whereas calcite normally would grow with a faceted morphology.

Nature also often combines properties of multiple compounds, creating composite materials that combine the best properties of their individual building blocks. Nacre is such a composite, consisting of aragonite crystals embedded in an organic matrix, and is found in the shells of e.g. abalones and other mollusks (Figure 1.3). On its own, the hard aragonite is brittle and would provide insufficient protection as it easily fractures. On the other hand, the organic matrix is too soft to provide any protection at all. However, building a composite of aragonite platelets imbedded in the organic matrix creates a hard shell, where the enveloping organic matrix limits crack propagation to an individual platelet. This results in a material with similar hardness to pure aragonite, but with a 3000 times higher toughness. Thus, also here nature’s careful organization of compounds gives its materials their fascinating properties.

Figure 1.3: A mollusk shell made of nacre. Its iridescent color and crack resistant properties are derived from aragonite platelets embedded in an organic matrix. Reprinted (adapted) with permission from Schäffer et al., Chem Matter 1997. © (2020) American Chemical Society.
1.3 Bio-inspired Materials

The remarkable properties of materials produced by nature have not gone unnoticed. In fact, whole research fields are dedicated to recreating these properties in manmade-materials.\textsuperscript{74–76} This bio-inspired approach allows particular combinations of properties to be realized, which would otherwise be difficult to make. For example, it is well-known that hard materials are often brittle, while tough materials are often soft.\textsuperscript{74,77} Yet, biominerals like bone and nacre are both hard and tough, because of their hierarchical ordering at the nano-to-microscale.\textsuperscript{44,60,68,69} And even if the biomineral breaks, the organism often has ways to repair it.\textsuperscript{67,78} Imagine the added benefit of these properties, if they could be incorporated into our own man-made materials.

Mimicking nature can be done in various ways.\textsuperscript{74} It is possible to only mimic one aspect, e.g. the structural layout that nature produces, and with this obtain similar properties with the imitation material.\textsuperscript{36,79} An example of this is directional freeze drying, which allows precise control over the morphology of the resulting nanocomposite.\textsuperscript{36,80} Here, a ceramic suspension is directionally frozen with lamellar ice crystals, which expels the ceramic particles. After removing the ice a homogeneous layered ceramic scaffold is obtained, with holes where the ice originally was. By filling these holes with a soft and tough material, a nacre-like material is formed with up to twice the toughness and hardness of natural nacre. Hence, even though the assembly is very different from what nature does, the resulting nanocomposite still retains the desired combination of hardness and toughness.

A bio-inspired approach can also mimic multiple aspects of nature, for example both the structural layout and the way of assembly. Here, additive manufacturing is an interesting example.\textsuperscript{81} In this technique materials are deposited in a layer-by-layer fashion, which shares many similarities to how nature builds materials.\textsuperscript{82–84} These common features include the supply of building blocks in a continuous or stepwise manner, a programming code dictating the shape and local composition of the to-form material, ways to convert this code into the structural layout of the material and ways to solidify the shape after the shaping process is done.\textsuperscript{82} By mimicking nature, materials can be produced with not only a programmable shape, but also with a tunable local structural layout.\textsuperscript{85,86} This has resulted in materials that for example mimic the toughness of nacre, but also in self-healing materials.\textsuperscript{87,88} Overall, this approach is believed to still have a lot of untapped potential that can bring us closer to understanding nature and its material design.

One system which mimics nature’s assembly and hierarchical layout is the co-precipitation of silica (SiO\textsubscript{2}) and earth alkali carbonates (CaCO\textsubscript{3}, SrCO\textsubscript{3}, or BaCO\textsubscript{3}) (See examples in Figure 1.4).\textsuperscript{89–96} It was originally discovered by the group of Garcia-Ruiz, who noted that growing BaCO\textsubscript{3} in the presence of SiO\textsubscript{2} resulted in intricate microshapes with morphologies uncommon for crystals.\textsuperscript{93,94} They dubbed these architectures ‘biomorphs’, as their nanocomposite layout and way of formation are very similar to those of biominerals. Yet, there is much more to these composites than only the way they form.\textsuperscript{97} In recent years, scientists have started to functionalize these biomorphs, highlighting their nanocomposite structural layout.\textsuperscript{98} Furthermore, their ability to be shaped also has drawn much attention, where the biomorphs act as chemically sculpted architectures.\textsuperscript{96,99} Thus, the term ‘nanocomposite’ or ‘architecture’ is better suited when describing the biomorphs structure and shape, respectively.
The procedure to make these nanocomposite architectures is remarkably straightforward (Figure 1.5A). In its simplest form, all that is required is a beaker containing an aqueous solution of barium ions (Ba\(^{2+}\)) and metasilicate (SiO\(_3\)\(^{2-}\)). Furthermore, placing a substrate in this solution gives the architectures a place to precipitate. Then, by simply waiting, carbon dioxide (CO\(_2\)) will diffuse from the air into the solution and initiate the co-precipitation. From an experimental perspective, the architectures can simply be retrieved from the solution after 1.5 hours.
From a mechanistic perspective, an intriguing process is taking place in these 1.5 hours. As the CO$_2$ is taken up by the solution, bicarbonate (HCO$_3^-$) is formed which reacts with the Ba$^{2+}$ (Figure 1.5B$_1$):

$$Ba^{2+}(aq) + HCO_3^-(aq) \rightarrow BaCO_3(s) + H^+(aq) \quad (1.1)$$

Here, BaCO$_3$ precipitates as nanocrystals near the meniscus of the solution, while locally forming protons (H$^+$) (Figure 1.5B$_2$). The locally lowered pH around the nanocrystals instigate the second precipitation:

$$SiO_3^{2-}(aq) + 2H^+(aq) \rightarrow SiO_2(s) + H_2O(l) \quad (1.2)$$

Here, SiO$_3^{2-}$ precipitates as SiO$_2$ and forms an isolating layer around the BaCO$_3$ (Figure 1.5B$_3$). This inhibits the growth of the BaCO$_3$, which can only grow further where the SiO$_2$ is not present (Figure 1.5B$_4$). This interplay between growth and inhibition gives the architectures its intricate shape.$^{93,94}$

![Figure 1.5: Illustrative overview of the co-precipitation of BaCO$_3$ and SiO$_2$. A, Experimental setup, which requires just an aqueous solution of Ba$^{2+}$ and SiO$_3^{2-}$. B, Schematic of the co-precipitation steps. 1, BaCO$_3$ forms when HCO$_3^-$ reacts with Ba$^{2+}$ (reaction 1.1). 2, During the formation of BaCO$_3$, the acidity increases locally. 3, SiO$_3^{2-}$ precipitates around the BaCO$_3$ because of the lowered pH (reaction 1.2). 4, BaCO$_3$ continues to precipitate on places that have not been overgrown with SiO$_2$, restarting the cycle.](image-url)
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**Figure 1.6: Precipitation-rate Graph and Sculpted Architectures.** A, SiO$_2$ precipitation (solid gray line) occurs in a very specific pH range, while BaCO$_3$ precipitation (dashed red line) occurs over a wider pH range. The full pH range of the graph is $\sim$ 8 to 12. B, Coral grown at the higher pH (1) crossing point. C, Spiral grown at the lower pH (2) crossing point. D, Vase grown with a CO$_2$-pulse. Graph (A) reprinted with permission from Noorduin et al., Science 2013. 96

The eventual shape of the architecture can be sculpted by manipulating growth parameters like pH, CO$_2$-concentration and temperature. 95,96 BaCO$_3$ precipitates steadily more with increased pH, whereas SiO$_2$ precipitates around a specific pH, and there exist 2 unique regimes where these precipitation rates cross each other (Figure 1.6A). 96 The co-precipitation proceeds around these two crossing points, and dictates the shape of the resulting nanocomposite architectures. In the case of the crossing point at higher pH (starting pH=11.8), the silica precipitates away from the bulk solution, causing the BaCO$_3$ to grow towards the solution, creating coral- and stem-like shapes (Figure 1.6B). At the lower crossing point (starting pH=11.2), the silica precipitates towards the bulk solution, causing the BaCO$_3$ to grow away from the solution, creating spiral- and leaf-like shapes (Figure 1.6C). As another example, the precipitation can also temporarily be favored for BaCO$_3$ with a CO$_2$ pulse, causing a stem-like shape to expand, which after the pulse only continues to grow at the edges as the center can not get enough building blocks, causing a vase-like shape to form (Figure 1.6D). These adaptations to the synthesis provide a simple, yet powerful way to shape the resulting nanocomposites.

1.4 Ion Exchange

Though bio-inspired co-precipitation is an intriguing method to shape nanocomposites in 3D, it also inherits a limitation from nature: Its composition choice is limited to silica and earth alkali metals. Yet, the structural layout of a nanocomposite could potentially overcome this limitation, because during the co-precipitation the BaCO$_3$ forms as nanocrystals. Nanocrystals have a high surface area and small volume, which makes them prone to ion exchange reactions. These reactions allow the shape of the crystal to be retained, while changing its composition by either replacing its cations (cation exchange), or anions (anion exchange). 100,101
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Cation exchange is a well-established process for individual nanocrystals, and the principles behind these exchange reactions have been rationalized from a thermodynamic perspective. In short, whether an ion exchange occurs can be estimated by comparing the association energy and solvation energy of the replacing and replaced compound. These values can either be calculated directly, or can be estimated from the solubility constants of these compounds for a given solution. For example, a cation exchange of a BaCO$_3$ nanocrystal to a new metal carbonate nanocrystal is likely to occur in water, as the solubility product of BaCO$_3$ in water ($5.1 \cdot 10^{-9}$) is much higher than for other metal carbonates like CdCO$_3$($5.2 \cdot 10^{-12}$), PbCO$_3$($7.4 \cdot 10^{-14}$) or CoCO$_3$ ($1.4 \cdot 10^{-13}$).

Anion exchange on the other hand is more difficult. Besides thermodynamic considerations, the local reaction conditions and diffusion rates are also crucial for anion exchange reactions in particular. Anions generally are larger than cations and diffuse slower, making them more difficult to remove from the crystal lattice. Fortunately, sometimes anion exchange can be assisted by other mechanisms occurring within the anion. Such is the case with carbonate anions, who decompose at elevated temperatures. During this decomposition, the crystal structure reorganizes, which can be used to change the morphology of individual nanocrystals and instigate anion reactions.

In this thesis we explore ion-exchange reactions performed on nanocrystals in self-assembled structures. To this aim we will first co-precipitate BaCO$_3$/SiO$_2$ into nanocomposites, and then develop ion exchange reactions that modify the chemical composition (Figure 1.7). Combined with the sculptable nature of the original BaCO$_3$/SiO$_2$ nanocomposites, this ion exchange potentially allows for a system where first a material is sculpted in a particular shape with co-precipitation, and then is converted to a new composition. This separates the shaping process from the eventual composition, combining bio-inspired assembly with the compound selection of manmade materials.

Figure 1.7: Schematic for performing ion exchange on nanocomposites as explored in this thesis. By performing ion exchange, we will attempt to exchange both the metal (from barium to target metal M) and the anion (from carbonate to target anion X) of the composite's nanocrystals.
1.5 Thesis Outline

In this thesis, we explore the possibilities of performing ion exchange reactions on BaCO$_3$/SiO$_2$ nanocomposites, as well as potential applications of the resulting nanocomposites.

In Chapter 2, we perform a case study on the conversion to CdS, with which we reveal the essential parameters of an ion exchange reaction. We then expand this case study to a general conversion plan, where we convert the nanocomposites to oxides and sulfides of cadmium, manganese, iron, nickel and cobalt. With this chapter, we establish the general parameters for an exchange reaction.

In Chapter 3, the nanocomposites’ applicability in catalytic processes is analyzed. First, nickel nanocomposites are employed for the dry reforming of butane. Here, the catalytic activity of these nanocomposites at (desirable) low temperatures is analyzed and compared to traditional catalysts. Second, the performance of cobalt nanocomposites in the Fischer-Tropsch process is investigated. Specifically, we show that the selectivity of the resulting products can be tuned by varying the composite’s nanocrystal grain size. Overall, this chapter shows that nanocomposites can act as catalysts with tunable parameters, and in some instances rival traditional catalysts.

In Chapter 4, we expand the conversion possibilities to non-transition metals and non-chalcogenides. For this, we first develop an exchange route to lead carbonate, a non-transition metal. The resulting nanocomposites are then converted to lead halide perovskites. This conversion demonstrates not only an anion exchange towards metal halides, but also the possibility of an ion insertion (specifically methylammonium). Furthermore, we investigate the luminescent properties of these perovskite nanocomposites, which combined with their sculptable 3D shape show potential for photovoltaic applications.

In Chapter 5, we investigate a conversion pathway without a carbonate intermediate. Specifically, we convert our nanocomposite architectures to tin, a metal without a stable carbonate, where the converted nanocomposite forms a tin oxy-hydroxide instead. This oxy-hydroxide intermediate possesses similar properties as a normal carbonate intermediate, and can readily be converted to both tin oxide and tin halide perovskite. This chapter shows that the cation exchange reactions performed on the nanocomposites are not limited to metal carbonates, and that many more pathways could still be discovered.

Overall, this thesis introduces an assembly/conversion system for nanocomposite architectures, where control over their shape and composition is separated in two steps. We first identify the essential mechanisms with a proof-of-principle system, where BaCO$_3$/SiO$_2$ nanocomposites are converted into CdS/SiO$_2$ nanocomposites, while preserving their shape. We then generalize this principle to a large diversity of iron, manganese, cobalt, nickel, cadmium, lead and tin salts. Finally, we demonstrate the potential of these converted nanocomposites in catalytic and optoelectronic applications, showing how an independent control of shape and composition opens exciting new ways to create functional materials.
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