

# Localized Light-Induced Precipitation of Inorganic Materials

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*This perspective is dedicated to the memory of Prof. Dr. Helmut Cölfen.*

The light-induced control in the fabrication of materials is a field in continuous development. So far, photo-induced processes have been used mostly for organic polymeric materials. However, there is a recent, increasing interest in exploring the possibility of using these techniques to induce the precipitation of inorganic materials. This perspective paper outlines the main

principles of the light-induced precipitation of inorganic materials, focusing on the recent papers published in this field. The description of the mechanisms and the materials involved in these light-induced processes highlight their many possibilities and future challenges, which could pave the way for significant advancements in this exciting technology.

## 1. Introduction

The spatial and temporal control of materials production represents the main aim for micro- and nanofabrication, field in continuous growth for many applications, from material science to medicine.<sup>[1]</sup> In this view, photolithography methods are at the basis of the most developed technologies.<sup>[2,3]</sup> Hence, light can induce chemical reactions with high spatial precision, since it can be focused in a defined area.<sup>[4]</sup> Also, for better chemical control, light intensity and frequency can be easily modulated, influencing photochemical reaction mechanisms.<sup>[5]</sup> A typical photolithography process involves a light source that is usually a laser or a LED focused lamp. The kind of irradiation source and its features define: 1) the irradiated area, and thus the resolution of the material to be produced, 2) the light distribution over time (pulsed or continuous sources and light intensity variation), and 3) the kind of process activated, based on the light wavelength. Light-induced chemical reactions often occur in a liquid precursor, which converts into a solid product

within the irradiated area through a photopolymerization or a photocrosslinking reaction.<sup>[2]</sup> The liquid precursor is mainly composed of monomers and a photoinitiator, which, once irradiated, induces the polymerization reaction through a radical mechanism.<sup>[6]</sup> The polymer that is formed, also called negative photoresist,<sup>[7]</sup> is insoluble in the reaction medium and, thus, precipitates instantaneously.<sup>[8]</sup> In particular, typical photoinitiators for UV-light are benzophenone, phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Irgacure 819), 2,4,6-trimethylbenzoyldiphenyl phosphine oxide (Lucirin TPO) etc,<sup>[6]</sup> whereas photoinitiators for visible light are mainly metal complexes, such as germanium, ruthenium or iridium complexes, and organic dyes, such as camphorquinone and anthraquinone derivatives.<sup>[9]</sup> Typical photoresists are acrylate monomers and PEG-based monomers;<sup>[10]</sup> consequently, the final materials fabricated by these processes are organic polymeric materials. However, many important applications are based on inorganic materials; thus, recently, researchers have focused their attention on new strategies to locally produce inorganic materials using light stimuli. The possibility of obtaining the formation of inorganic materials with precise structure and spatial confinement can bring significant improvements to many fields, such as materials science, electronics, medicine, energy, and environment.<sup>[11]</sup> The purpose of this perspective is to outline a new field in photo-induced nano- and micro-fabrication that focuses on the local formation of inorganic materials. This field is currently little explored, with still not much literature among papers and patents.<sup>[12]</sup> Here, we are going to describe the main papers on this topic, which deal with the light-triggered precipitation of carbonates and phosphates. For example, Menichetti and co-workers developed the photo-precipitation of CaCO<sub>3</sub> and SiO<sub>2</sub>/BaCO<sub>3</sub> biomorphs, inorganic-inorganic composite materials whose morphologies resemble the ones of living organisms.<sup>[13–15]</sup> The exact mechanism led to the development of a very precise photo-precipitation study of SiO<sub>2</sub>/BaCO<sub>3</sub> biomorphs, described in the papers of Bistervels et al.<sup>[16,17]</sup> Additionally, Besirske and co-workers studied the photo-precipitation of calcium phosphate

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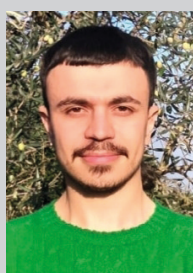
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structures.<sup>[18]</sup> Finally, Bistervels et al. developed a new precipitation method based on NIR instead of UV-light, by which they locally controlled the crystallization of carbonate and phosphate salts.<sup>[19]</sup> The five papers cited above represent the first examples of spatially controlled light-induced formation of inorganic salts. This perspective will define the main points of these works and compare them based on the concept, the mechanisms, the materials obtained and the future perspectives, describing the basis of this new technology, applicable for many other inorganic materials in the future.

## 2. Fundamentals of the Technique

In the papers cited in the introduction section,<sup>1</sup> the main aim has been to study the local light-induced precipitation of an inorganic material from a liquid precursor. Based on the final scope of each work, this principle was developed in different ways. Here, the kind of inorganic materials to be formed were calcium carbonate, witherite-silica biomorphs and calcium phosphates. The paper in which Menichetti et al. developed the light-induced formation of CaCO<sub>3</sub> aimed to obtain structures in the optics of micro- and nanofabrication techniques,<sup>[13]</sup> thus focusing on an efficient process using cheap and harmless light

sources. They also employed a similar light-induced mechanism to achieve CaCO<sub>3</sub> local dissolution, focusing on artwork restoration.<sup>[20]</sup> Besirske et al. presented a proof of principle on calcium phosphates photo-precipitation to find a possible application for dental repair<sup>[18]</sup> and thus obtain biomimetic materials similar to the body's own materials. In addition to the precipitation of pure carbonates or phosphates, Menichetti et al. also started to study the photo-induced precipitation of silica/carbonate biomorphs. This highlights another aspect of the investigation on the precipitation of inorganic materials with light: the possibility of studying nucleation processes in a very detailed manner. This is what the paper of Bistervels et al.<sup>[16]</sup> has focused on: authors have followed the formation of biomorphs aiming to obtain a very precise control on the shaping of their structures.<sup>[17]</sup> In parallel, the same authors provided an additional version of the light-induced precipitation technique.<sup>[19]</sup> While in the previous cases the formation of the inorganic materials was induced by photochemical reactions that implied the degradation of a photoactive molecule, in the last case the precipitation was induced by heating, provided with NIR laser irradiation. This represents a new mechanism by which the authors studied the formation of carbonate and phosphate salts, controlling the growth of single crystals and selecting their polymorphs.



Dario Mordini is attending a PhD program in "Nanoscience for medicine and the environment" and he is working in the Marco Montalti's group. He got a M.Sc. in "Photochemistry and molecular materials" defending a thesis on the control of the morphological and optical properties of inorganic hybrid nanostructure. Currently, his research is focused on the use of melanin derivatives for photocatalysis and cosmetic application.



Marco Montalti is Professor of Chemistry at the department "Giacomo Ciamician" entitled to one of the first photochemists and a visionary of the solar energy utilization. MM research is mostly devoted to the design of environmentally friendly and biocompatible nanomaterials, also derived from natural or biomimetic melanin and to the investigation of their interaction with light. Applications involve photocatalyst, imaging, nanomedicine, and cosmetics.



Patricia Besirske is a PhD candidate who started her studies in the group of the late Professor Helmut Cölfen and is currently completing her thesis under the supervision of Dr. Cristina Ruiz-Agudo. She received her BA and MA in NanoScience from the University of Konstanz. Her research interests include the synthesis of light-splittable organic molecules suitable for the precipitation of calcium phosphates, the study of these crystallization processes, and the combination of organic and inorganic chemistry to advance 3D printing technologies.



Arianna Menichetti obtained her PhD in 2021 under the supervision of Prof. Marco Montalti at the University of Bologna. She is currently researcher at the Department of Chemistry "Giacomo Ciamician" of the University of Bologna. Her research interests include photochemistry and nanomaterials, with applications in photocatalysis, photoinduced material patterning, art restoration and cosmetics.



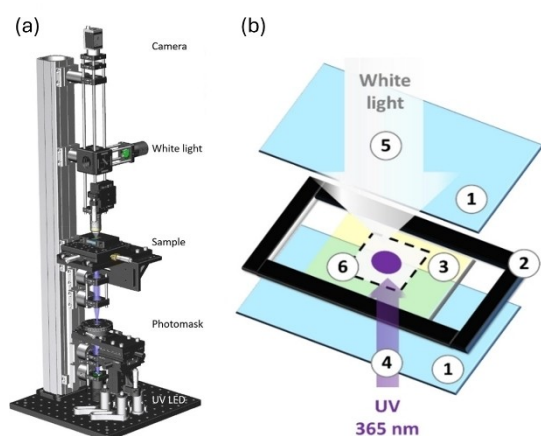
Juan Manuel García-Ruiz is Ikerbasque Professor at the Donostia International Physics Center and an Emeritus Research Professor at CSIC. He is an expert in the crystallization of minerals, drugs, and proteins. Currently, his main field of study is the phenomena of self-organization in biological and geological structures, with implications for the origins of life, primitive life detection and the manufacture of new materials.

In this section, we are going to discuss in detail the different mechanisms that have been investigated to precipitate inorganic materials through light irradiation with spatial precision. In particular, the liquid precursors were injected into crystallization cells, then placed in an inverted optical microscope (Figure 1). Finally, the mineralization was induced by irradiation in spatial confined spots.

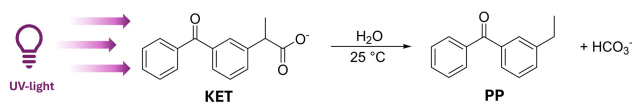
The common idea was to design a liquid formulation containing the precursors of mineral-like materials, in which irradiation would trigger the material precipitation by overcoming its solubility limit. Solubility, and thus precipitation, can be controlled by adjusting parameters like solute concentration and temperature,<sup>[21,22]</sup> and these principles are at the basis of the precipitation mechanisms described below.

## 2.1. Light-Induced Control on Supersaturation

As mentioned above, precipitation can be induced by an increase of solute concentration. Here, the idea was to exploit photochemical reactions that induced the formation of ions in solution while irradiated, overcoming the saturation limit of the final material.<sup>[23]</sup> Menichetti et al. used the ketoprofen anion (KET) to photo-precipitate either calcium carbonate or witherite-silica biomorphs in alkaline solution,<sup>[13]</sup> the latter mineral-



**Figure 1.** (a) Setup used by Bistervels et al. for the photo-precipitation of witherite-silica biomorphs (Adapted with permission from ref.<sup>[17]</sup> Copyright 2024 The Royal Society of Chemistry). (b) Setup of the crystallization cell used by Menichetti et al. for the photo-precipitation of calcium carbonate.<sup>[13]</sup> The cell was assembled by (1) two glass slides and (2) a rubber spacer (0.1 cm thick), then (3) the liquid precursor was injected into the cell, and the system was sealed. (4) A LED light source ( $\lambda = 365$  nm) was used to induce the photo-precipitation, while (5) a white light was used to detect the time-lapsed images of (6) the selected area (Adapted with permission from ref.<sup>[13]</sup> 2021 Wiley-VCH GmbH).

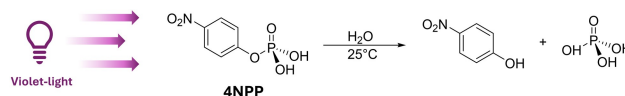


**Figure 2.** Photo-decarboxylation reaction of KET once exposed to UV-light irradiation. Bicarbonate ions ( $\text{HCO}_3^-$ ) and 3-ethylbenzophenone (PP) are produced.

ized also by Bistervels et al. with the same approach.<sup>[19]</sup> KET is a water-soluble molecule that undergoes photo-decarboxylation upon UV irradiation.<sup>[24]</sup> Hence, the photochemical reaction leads to the formation of bicarbonate ( $\text{HCO}_3^-$ ) in alkaline solution and an insoluble by-product, 3-ethylbenzophenone (PP)<sup>[25]</sup> (Figure 2).

In strongly alkaline aqueous solutions,  $\text{HCO}_3^-$  quickly converts into carbonate ( $\text{CO}_3^{2-}$ ), which, in the presence of metal cations, leads to the precipitation of sparingly soluble carbonates.<sup>[26]</sup> Therefore, the liquid precursor contained alkaline-earth metal cations, like  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ , to precipitate carbonate minerals with the  $\text{CO}_3^{2-}$  photo-release. Herein, it is important to stress that metal cations and KET concentrations should be well balanced to avoid precipitation without irradiation. Furthermore, the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  concentration could be adjusted by tuning the irradiation intensity, leading to better control of the mineralization processes. Indeed, Menichetti et al. demonstrated that the nucleation density of witherite-silica biomorphs is dependent on the intensity of the irradiation: the higher the intensity of the irradiation, the higher the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  concentration in the irradiated spot, which induces the nucleation of a more significant number of microstructures in the irradiated area. In the same way, Bistervels et al. explored how micro-patterning spatial resolution can be improved by adjusting light intensity. Indeed, to avoid precipitation outside the irradiated spot,  $\text{HCO}_3^-/\text{CO}_3^{2-}$  diffusion should be avoided. This can be achieved by increasing the irradiation intensity in a reduced selected spot, accelerating the formation of the ions and their precipitation before they have time to diffuse outside the selected area. With light intensity modulation, they also managed to control nucleation, growth and morphology, parameters strongly influenced by  $\text{HCO}_3^-/\text{CO}_3^{2-}$  concentration gradient in such fascinating microstructures.<sup>[27,28]</sup> Carbonate-based materials are not the only ones that have been photo-precipitated. For example, Besirskic et al. proposed an analogous method to induce the local mineralization of calcium phosphate.<sup>[18]</sup> Herein, the selected photolabile precursor was 4-nitrophenylphosphate (4NPP), which releases phosphoric acid ( $\text{H}_3\text{PO}_4$ ) in solution when it is irradiated by UV light (Figure 3).

In alkaline solution,  $\text{H}_3\text{PO}_4$  deprotonates into the phosphate ion ( $\text{PO}_4^{3-}$ ). When  $\text{Ca}^{2+}$  ions were also added to the formulation in an open-air atmosphere, the formation of solid amorphous carbonate hydroxyapatite type B ( $\text{Ca}_{10-x}[(\text{PO}_4)_{6-2x}(\text{CO}_3)_{2x}](\text{OH})_2$ ) was observed. Moreover, this process was performed in a gel matrix, which Menichetti et al. had already anticipated in the  $\text{CaCO}_3$  precipitation, to limit diffusion and obtain fixed structures.



**Figure 3.** Photo-cleavage reaction of 4NPP once exposed to UV-light irradiation.

## 2.2. Light-Induced Control on Temperature

Temperature is another parameter affecting the solubility of minerals. It is well known that, for certain salts, the solubility increases with temperature, while in other cases, it decreases. In the photo-precipitation system, temperature fluctuation can be tuned using NIR light since, in this spectral range, the photon energy induces the stretching/bending of water bonds<sup>[29]</sup> with subsequent heat dispersion. Hence, the rapid temperature increase induces the precipitation of salts with retrograde solubility.<sup>[30]</sup> An example of this process is given by Shi et al., which achieved the precipitation of  $\text{CaCO}_3$ .<sup>[22]</sup> Alternatively, Bistervels et al. managed to crystallize bio-relevant compounds ( $\text{CaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{BaCO}_3$ ,  $\text{SrSO}_4$  and bone mineral hydroxyapatite) with this method by equipping a NIR laser light ( $\lambda = 1435 \text{ nm}$ ) to an optical microscope,<sup>[19]</sup> resulting in a local control of the process. Water-soluble salts containing the ions of interest were dissolved in an aqueous solution without overcoming the solubility limit of the desired mineral. Sodium chloride was also dissolved into the formulation to raise the solubility limit of the other salts, allowing an increase in the concentration of precursors. The quick local temperature elevation led to precipitation in the irradiated spot, with a high spatial-temporal control. Furthermore, high-intensity irradiation was exploited to induce nucleation, while less-intense irradiation was selected to induce crystal growth.

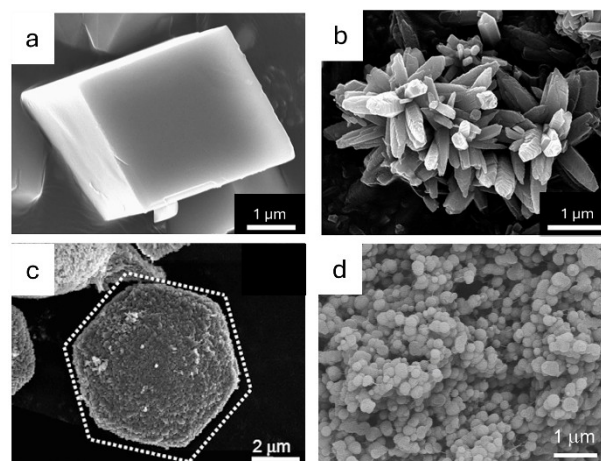
## 3. Inorganic Materials obtained by Photoreactions

This section describes the inorganic materials synthesized through photo-precipitation mechanisms. In more detail, we are going to show how the crystallographic properties of the minerals can be tuned by adjusting the experiment's setup and how the morphology of the patterning can be selected by setting the intensity of radiation.

### 3.1. $\text{CaCO}_3$ , $\text{SrCO}_3$ and $\text{BaCO}_3$

Among inorganic materials,  $\text{CaCO}_3$  is the main component in relevant biological structures<sup>[31]</sup> and finds plentiful applications in industries such as agriculture, medicine, building, and artworks.<sup>[32]</sup> From a mineralogical point of view,  $\text{CaCO}_3$  can crystallize in three different anhydrous polymorphs: calcite, the most thermodynamically stable form, aragonite and vaterite.<sup>[33]</sup> However, even precipitation of the amorphous calcium carbonate (ACC) is possible (Figure 4).<sup>[26]</sup>

Regarding photo-precipitation technologies, Menichetti et al. mineralized  $\text{CaCO}_3$  in solution and gel upon light irradiation thanks to the photo-decarboxylation of KET.<sup>[13]</sup> The material was crystalline, showing the typical rhombohedral shape of calcite and the characteristic hexagonal shape of vaterite.  $\text{CaCO}_3$  was also precipitated by Bistervels et al. by exploiting the retrograde solubility of this chemical



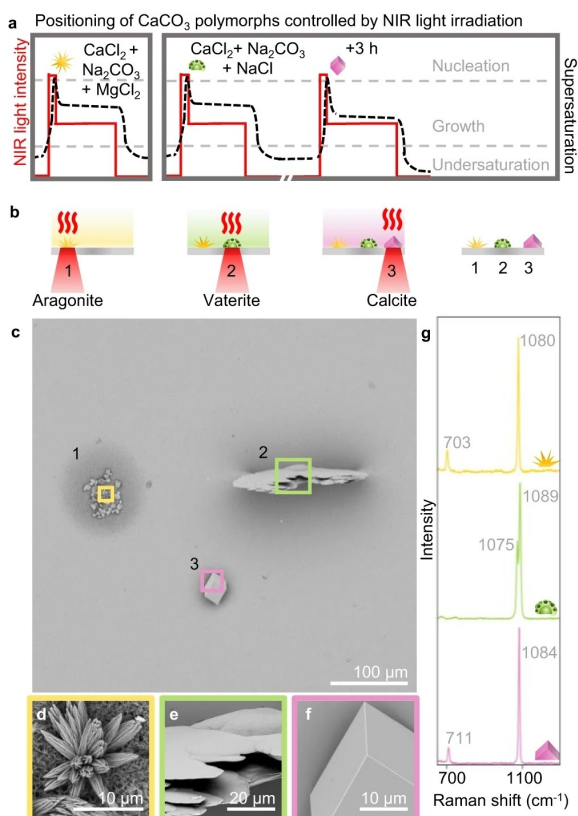
**Figure 4.** SEM images of  $\text{CaCO}_3$  polymorphs: (a) calcite, (b) aragonite (Adapted with permission from ref.<sup>[34]</sup> Copyright 2016 Springer Nature) (c) vaterite (Adapted with permission from ref.<sup>[35]</sup> Copyright 2012 American Chemical Society) and (d) ACC (Adapted with permission from ref.<sup>[36]</sup> Copyright 2013 American Chemical Society).

compound.<sup>[19]</sup> They demonstrated that control over the polymorphism can be achieved. Indeed, they were able to precipitate single crystals of aragonite, vaterite and calcite in a triangular pattern (Figure 5). Aragonite crystal was obtained by adding  $\text{Mg}^{2+}$  ions to the formulation, then vaterite crystal was precipitated irradiating a freshly prepared precursor solution, in  $\text{CaCO}_3$  high supersaturation conditions. Finally, the same solution was left equilibrating for three hours to allow, once irradiated, the precipitation of calcite. Another important example of polymorph selection is given by Shi et al., who selected  $\text{CaCO}_3$  polymorphs tuning for light-induced temperature increase.<sup>[22]</sup>

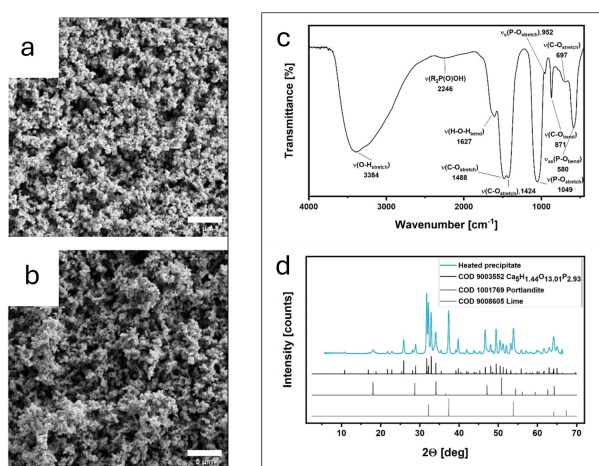
In addition to that, photo-precipitation tests were performed to demonstrate that this technology was suitable for other carbonates, such as strontianite  $\text{SrCO}_3$  and witherite  $\text{BaCO}_3$ .

### 3.2. Calcium Phosphates

Calcium phosphates are highly studied for biomedical applications, like the design of scaffolds, bone cement and toothpastes.<sup>[37]</sup> Unfortunately, in the 3D printing of medical devices, ceramic materials are not easy to process, thus photo-curable formulations still need a percentage of polymeric content.<sup>[38]</sup> For this reason, the method proposed by Besirskic et al., which managed to precipitate carbonated hydroxyapatite (CHA) through photochemical reactions,<sup>[18]</sup> could be an alternative way to overcome this issue. The mineral precipitates in its amorphous phase, which is preferred in bio-medical applications since it is more osteoconductive than its crystalline form, with a homogeneous size of the particles (Figure 6a,b). Also, the degree of carbonation was tuned by controlling the  $\text{CO}_2$  content in the system and upon heating treatment ( $1000^\circ\text{C}$ ), and the material was converted into a crystalline



**Figure 5.** (a) Schematic representation that described the composition of the liquid formulation and the irradiation process used for the photo-precipitation using the working conditions of Bistervels et al. (b) Schematic representation that shows the obtained polymorphs (1. Aragonite, 2. Vaterite and 3. Calcite). (c) SEM images of mineralized  $\text{CaCO}_3$ , (d) aragonite, (e) vaterite and (f) calcite, respectively. (g) Raman-spectra of the photo-precipitated crystals, aragonite (yellow line), vaterite (green line) and calcite (pink line) (a–f Reused with permission from ref.<sup>[19]</sup> Copyright 2023 Springer Nature).



**Figure 6.** SEM images of the photo-precipitated CHA (a) pre-heating and (b) post-heating (scale bar 5  $\mu\text{m}$ ). (c) IR spectrum of the photo-precipitated CHA. (d) X-ray diffractograms of photo-precipitated CHA post-heating, and the reference compounds (crystalline CHA,  $\text{Ca}(\text{OH})_2$  and  $\text{CaO}$ ). (Adapted with permission from ref.<sup>[18]</sup> Copyright 2023 Wiley-VCH GmbH).

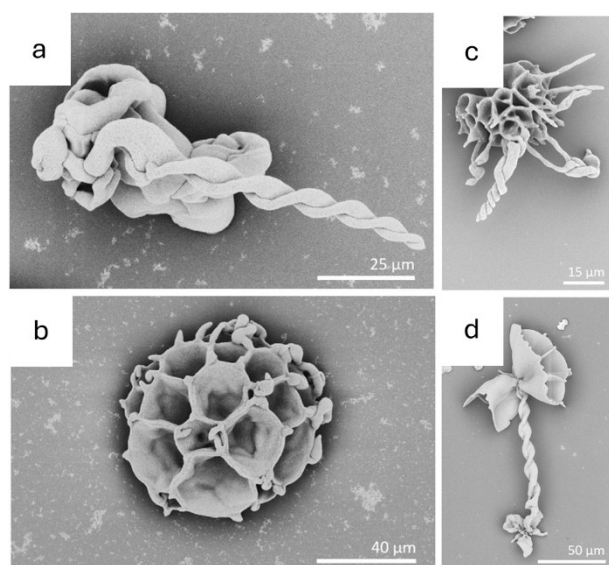
mixture, mainly composed of crystalline CHA,  $\text{Ca}(\text{OH})_2$  (portlandite), and  $\text{CaO}$  (lime) (Figure 6c,d).

Bistervels et al. managed to precipitate calcium phosphates through photo-thermal processes.<sup>[19]</sup> As in the case of carbonates, they exploited the retrograde solubility of this salt to photo-precipitate it. In this case, they added  $\text{NaCl}$  to the liquid formulation to avoid the precipitation of the amorphous phase of calcium phosphate, and they obtained crystalline calcium phosphate without additional thermal treatment.

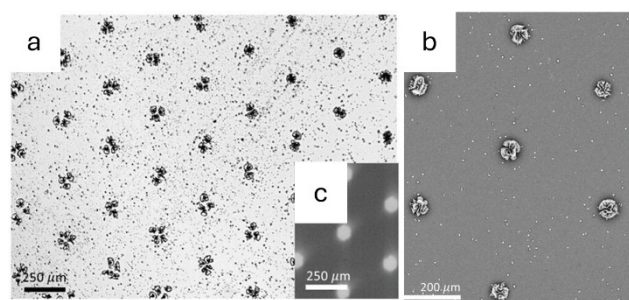
### 3.3. Witherite-Silica Biomorphs

Witherite-silica biomorphs are self-assembled microstructures that mineralize in alkaline conditions by co-precipitating crystalline witherite ( $\text{BaCO}_3$ ) and amorphous silica ( $\text{SiO}_2$ ).<sup>[15]</sup> They display a highly organized hierarchical orientation of the crystals in the internal part, coated by a silica shell.<sup>[27]</sup> In addition, the overall shape is curvilinear and sinuous, similar to helixes, caterpillars, flat sheets and corals.<sup>[39]</sup> All these features make this material very close to the one of biominerals, even if they are mineralized in abiotic conditions. Concerning the topic of this perspective, also witherite-silica biomorphs were successfully precipitated via light irradiation. Menichetti et al. achieved this aim by photo-releasing  $\text{HCO}_3^-$  from KET in an aqueous mixture of barium chloride ( $\text{BaCl}_2$ ) and sodium silicate ( $\text{Na}_2\text{SiO}_3$ ).<sup>[13]</sup> Interestingly, they obtained different morphologies depending on the intensity of light irradiation. Homogenous populations of witherite-silica biomorphs with a fake mitosis-like morphology and with a coral-like shape were mineralized, simply by tuning the power of the light source. Following the same principle, Bistervels et al. also demonstrated that different morphologies can be precisely distinguished by tuning the intensity of radiation during biomorph growth. Low-intensity irradiation induced the precipitation of helix-like biomorphs, while higher-intensity irradiation led to the development of coral-like biomorphs<sup>[17]</sup> (Figure 7a–d). A possible explanation for this is that, tuning the light power, we can also control the gradient of  $\text{HCO}_3^-$  concentration released by KET. In this way, they were able to select a specific mineralization mechanism instead of another.

In addition, Bistervels et al. explored new ways concerning the KET-assisted photo-precipitation of witherite-silica biomorphs.<sup>[16]</sup> They demonstrated that specific morphologies can be selected by setting a well-defined pH value. For example, helix-like biomorphs had grown at pH 10.8, while coral-like biomorphs had precipitated at pH 11.8. They not only selected the desired shape, but also the growth area. Applying a perforated mask between the irradiation source and the sample, witherite-silica biomorphs grew only in the irradiated spots, without any diffusion outside the area of interest (Figure 8a–c). They also obtained biomorphs with the boundary shape of triangles, spheres, and crosses.



**Figure 7.** SEM images of photo-precipitated witherite-silica biomorphs with different morphologies: (a) helix, (b) coral-like and (c,d) combined helix and coral morphology. (Adapted with permission from ref.<sup>[17]</sup> Copyright 2024 The Royal Society of Chemistry).



**Figure 8.** (a) Optical microscope images and (b) SEM images of a photo-induced micropatterning of coral-like witherite-silica biomorphs. (c) Optical microscope of the mask used in the micro-patterning. (Adapted with permission from ref.<sup>[16]</sup> Copyright 2021 Wiley-VCH GmbH)

#### 4. Future Perspectives

The literature published so far on this novel precipitation technique already proves its potential in different fields of application. There is, indeed, plenty of room to improve and apply this new technology.

One of the potential aspects of the light-induced precipitation technique is the possibility of controlling the morphology and the crystal phase of the obtained material through the light stimulus. This was demonstrated with two main effects: the light intensity can tune the concentration of the forming ions or the temperature of the irradiated area. It has already been demonstrated that it is possible to switch the morphology (either biomorphic or classical crystallographic) and texture (either single crystals or polycrystalline) during the precipitation of monohydrocalcite ( $\text{CaCO}_3$ ) building a single particle.<sup>[40]</sup> This feature has great potential for the construction of polymorphic mineral architectures. A recent example of this was given by Shi et al.,<sup>[22]</sup> who obtained multi-polymorphic  $\text{CaCO}_3$  crystal arrays

on a substrate, tuning the temperature through the photo-thermal effect. In this work the temperature variation was applied, irradiating the whole substrate and alternating it with temperature cooling. However, the light-induced precipitation technique has the advantage of acting locally, inducing a transformation in a defined area. This would allow the obtaining of polymorphic architectures with alternation of polymorphs on a microscopic scale and with high resolution. This would generate new libraries of materials in which there would be a combination of different polymorphs in an ordered superstructure. These new materials could lead to different properties with respect to the single polymorphs, and could be obtained just starting from the chemistry of a single material and in the absence of any additives.

A problem observed when inducing the local precipitation of minerals with light is the problem of the fixation of the precipitate. This is particularly challenging when drawing micro-patterns or building complex three-dimensional structures. The reason is that the heating and the concentration changes, which trigger precipitation, create Marangoni and thermal-driven convective fluid that removes the precipitate from their initial location, destroys patterns and even redissolves the precipitates. The first attempts at fixing the structure obtained were investigated in the works of Menichetti et al.<sup>[13]</sup> and Besirke et al.<sup>[18]</sup>, who used a gel matrix to fix the structures. However, the use of gels needs improvement, which could focus on controlling gel pores to prevent diffusion and act as a further constraint for local precipitation. Alternatively, structure fixation could be achieved by functionalizing the substrate with an agent that would promote or inhibit the precipitation of the material in an ordered pattern. Developing a proper fixation technique is very important because it paves the way for the obtaining of 3D mineral structures, as it is done with polymeric materials in the 3D printer. This would lead to a possible scaling-up of the photo-precipitation technique, maintaining the precision that is characteristic of this method. Indeed, the possibility of printing 3D structures of inorganic materials, potentially also on a large scale, would lead to improvements for many applications, from material to biomedical engineering.

In this review, we have summarized the state of the art of the photo-precipitation technique, which has been so far demonstrated for alkaline earth carbonates and calcium phosphates. However, this technique could be, in principle, applied to many other materials provided they have a solubility dependence on temperature, pH or redox state. For example, it would be interesting to investigate the light-induced formation of metals and semiconductors, tuning their properties based on the structure obtained. Also, the light-induced precipitation of composite materials could be achieved using orthogonal light stimuli. The investigation to explore the use of the technique to control the local precipitation of new materials should be based on: 1) the mechanism used to achieve precipitation, 2) the molecules that trigger the precipitation event (i.e. photo-initiators with the proper functional groups); 3) the solubility properties of the material in the medium. Then, coupling this approach to the improvements concerning the efficiency and safety of the mechanism and the properties of the obtained

material would contribute to enlarging the use of this technology.

## Acknowledgements

The authors thank the European Research Council for funding project 101069348 – INPATT. AM thanks “Network 4 Energy Sustainable Transition—NEST” (European Union—NextGenerationEU), project code PE000021. Open Access publishing facilitated by Università degli Studi di Bologna, as part of the Wiley - CRUI-CARE agreement.

## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

**Keywords:** Light-induced crystallization · Inorganic materials · Photochemistry · Patterning · Photolithography

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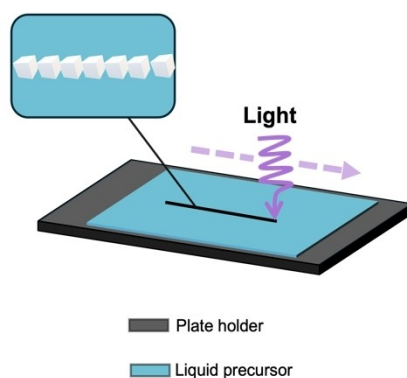
Manuscript received: July 17, 2024

Revised manuscript received: October 7, 2024

Version of record online: ■■■, ■■■

## PERSPECTIVE

A new field in photoinduced micro- and nanofabrication is currently evolving, consisting of the use of a light stimulus to precipitate inorganic materials with high local control. The technique has been recently developed to precipitate alkaline-earth metal carbonates and calcium phosphates, and it represents a powerful innovation for many applications in material science.



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**Localized Light-Induced Precipitation of Inorganic Materials**