

FACET

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dutch association for crystal growth



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FACET

Newsletter of the Dutch

Association for Crystal Growth

(DACG), section of the KNCV and

the NNV.

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1972 – 2022
50 years DACG

DACG board

[Dr. Carmen Guguta](#) (Technobis) chairperson

[Prof.Dr. Antoine van der Heijden](#) (TUD) secretary

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Cover figure



Hillocks on a GaAs (111)-surface grown from the gas phase via metalorganic chemical vapour deposition (MOCVD).

Image Radboud University / Hans te Nijenhuis.

From the editor

In 2022 DACG has existed for 50 years! Due to Corona our 50-year jubilee is postponed to 2023, but in 2022 there will be some celebrations. The first being a special mini-issue of NTVN this summer on crystal growth.

After two years of online meetings, we will soon see each other face to face. Our spring symposium will be held at AMOLF in Amsterdam on Wednesday May 25th! Here is the [link](#) for signing in.

In the annual meeting in October 2021 Dr. Carmen Guguta was welcomed to the DACG board. The board voted her in as the chairperson. Dr. Pieter Vonk was thanked for his 13 years as board member, of which the last as treasurer. The board voted Dr. Hans te Nijenhuis in as the new treasurer.

As always, it is easy to contribute to the FACET: recently published articles and theses, photos for cover figure, relevant announcements, ... Contributions may be delivered by [e-mail](#). Your ideas are welcome, please notify the editor: Marketta Uusi-Penttilä

Marketta Uusi-Penttilä

Upcoming events

- DACG Spring Meeting, 25 May 2022, AMOLF, Amsterdam.
 - DACG Fall Meeting, Oct 2022, TBD
 - 50-year jubilee, March 2023
-

Short introduction of Dr. Carmen Guguta

Dr. Guguta was elected for the DACG board in the annual meeting in October 2021. The board then chose her as the chairperson.

18 years of experience in pharmaceutical development cycle, from discovery to formulation, covering small molecules, drug substance and drug product. Deep experience in solid state chemistry. Previously worked with Avantium and Crystallics, contract research organizations.

Holds a PhD degree in Pharmaceutical Solid-State chemistry from Radboud University Nijmegen, The Netherlands.

Currently Dr. Carmen Guguta is the Global Head of Business Development & Marketing at Technobis Crystallization Systems, leading a team of highly skilled and experienced scientists and marketers. Her team focuses on unlocking new markets and market segments by developing new applications and establishing new collaborations.



Annual membership fee 2022

Just a friendly request for all members to check that you have paid your membership fee for 2022. Being a member you can participate our symposia for a reduced price.

The membership fee in 2022 is € 15 for professionals, € 10 for 65+ and € 5 for (PhD) students. Please mention "DACG membership fee 2022" in your payment.

The bank account of the NVKG is:
Ned. Ver. Van Kristal Groei.
NL60INGB0004305158

The annual membership runs from 1 January 20XX to 31 December 20XX.

Participating in the spring symposium paying the full participation fee includes the membership for that year (20XX); participating in the fall symposium paying the full participation fee includes the membership of the following calendar year (20XX + 1).

Report DACG symposium 8 October 2021

On 8 October, 2021, the DACG organized its fall meeting. This was the third time in a row that we organized an event online due to the COVID19 measures. The DACG symposium was attended by 38 participants. Hans te Nijenhuis opened the symposium and welcomed the participants. He extended a special welcome to the family of Gerda van Rosmalen, who passed away on 18 January 2021. Following the opening, Marloes Bistervels (AMOLF) gave an update on the Young-DACG initiative. A Telegram group has been initiated to quickly exchange questions, news, etc. among PhD students. A LinkedIn group is proposed for exchange of more basic information.



In remembrance of Gerda van Rosmalen, professor of Industrial Crystallization and Clean Technology at the Delft University of Technology from 1987-2002, Gerda's contributions to the national and international crystallization community were shared by Antoine van der Heijden and Herman Kramer (both TU Delft). Burak Eral (TU Delft) presented new achievements on steering crystallization with light, flow and soft matter. Carmen Guguta (Technobis), our new chair, introduced herself and presented on the possibilities to investigate crystallization kinetics using small scale crystallizers.

On behalf of Gerda's family, Koos Jansen acknowledged the DACG for the opportunity to participate in this symposium. Hans te Nijenhuis closed the symposium, expressing the hope to meet each other at an in-person event again in 2022.

Antoine van der Heijden



DACG Symposium

AMOLF, Amsterdam, 25 May 2022

1972 – 2022
50 years DACG

- 09:30 – 10:00 **Registration and coffee**
- 10:00 – 10:15 **Welcome and introduction**
 Carmen Guguta (DACG) / Wim Noorduin (host)
- 10:15 – 10:45 **Light-directed crystallization**
 Marloes Bistervels (AMOLF)
- 10:45 – 11:15 **Elucidating the effect of hyaluronic acid on the structure and morphology of calcium oxalate crystals**
 Sevgi Polat (Delft University of Technology)
- 11:15 – 11:45 **Probing the dynamic nature of calcite-electrolyte interface using atomic force microscopy**
 Saravana Kumar (University of Twente)
- 11:45 – 12:15 **Dendritic growth of nanoislands on Pt(111)**
 Francesc Valls Mascaro (Leiden University)
- 12:15 – 14:00 **Speed-dating, lunch + posters**
- 14:00 – 14:30 **The asymmetrical dependence on $\{Ba^{2+}\};\{SO_4^{2-}\}$ of $BaSO_4$ crystal nucleation and growth in aqueous solutions: a dynamic light scattering study**
 Sergej Seepma (Utrecht University)
- 14:30 – 15:00 **Floppy hydrated microcrystals**
 Rozeline Wijnhorst (University of Amsterdam)
- 15:00 – 15:15 **Coffee break**
- 15:15 – 15:30 **KNCV Piet Bennema Award for Crystal Growth 2021**
 Announcement prize winner by Rob Geertman (on behalf of jury); “honorable mention” for other 2 PhD students nominated for this award
- 15:30 – 16:15 **Anaerobic calcium phosphate granulation**
 Ricardo Cunha (Institute of Energy and Environmental Technology, Duisburg, Germany), prize winner of the KNCV Piet Bennema Award for Crystal Growth 2021
- 16:15 – 17:30 **Drinks / nibbles**

Venue: AMOLF, Science Park 104, 1098 XG Amsterdam

Registration: <https://amolf.nl/dacg>

Recent publications

- I. Baglai, S.W. van Dongen, M. Leeman, R.M. Kellogg, B. Kaptein, W.L. Noorduin, [Counteracting Enantiospecific Behavior of Tailor-Made Additives During Chiral Symmetry Breaking: Growth Inhibition versus Solid-Solution Formation](#), *Israel Journal Chemistry**, **2021**, 61, 1–6.
<https://doi.org/10.1002/ijch.202100086>

*special issue in honor of the 2021 Wolf prize in Chemistry for Prof. Lahav and Prof. Leiserowitz

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All biological systems are composed of molecules of a single chirality. Although many different scenarios can lead to chiral symmetry breaking, the transmission of the absolute configuration of one compound to another one remains challenging. We here demonstrate that during crystallization-induced chiral symmetry breaking by Viedma ripening, a cascade of different and counteracting processes can occur: solid-solution formation and dissolution inhibition favor symmetry breaking towards the same absolute configuration, while enantioselective growth inhibition favors symmetry breaking towards the opposite absolute configuration. These insights offer a new playground for controlling symmetry breaking processes that are of fundamental and practical importance.

- G. Grimaldi, D. Anthony, L. Helmbrecht, A. van der Weijden, S. van Dongen, I. Schuringa, J. Borchert, E. Alarcón-Lladó, A. Rao, W. L. Noorduin, B. Ehrler, [Microstructuring of 2D perovskites via ion-exchange fabrication](#), *Applied Physics Letters*, **2021**, 119, 223102.
<https://doi.org/10.1063/5.0065070>

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- Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam 1090 GD, The Netherlands

In recent years, two dimensional (2D) perovskites have attracted growing interest as a material for optoelectronic applications, combining the defect tolerance and strong absorption of bulk perovskites with enhanced material stability. Moreover, the possibility to tune their bandgap via control of the thickness of the perovskite layers allows precise optimization of the energy levels in these materials, making them ideal candidates for rationally designed semiconductor heterojunctions. However, despite the advances in the synthesis of 2D perovskites, typical fabrication strategies produce either uniform thin-films or isolated single crystals, severely hindering the prospect of patterning these materials. We demonstrate an ion-exchange synthesis of 2D perovskites, starting from a lead carbonate host material and converting it to 2D perovskites via a solution-based treatment. The process allows for the fabrication of 2D perovskites spanning a range of halide compositions and 2D layer thicknesses and yields highly crystalline luminescent materials. We demonstrate the potential of this approach for 2D perovskite patterning, spatially localizing 2D perovskite structures via the conversion of pre-patterned lead carbonate structures. These results significantly expand the

possibilities of 2D perovskite material design toward controllable integration of 2D perovskites in complex device architectures.

- M.H. Bistervels, M. Kamp, H. Schoenmakers, A.M. Brouwer, W.L. Noorduin, [Light-controlled nucleation and shaping of self-assembling nanocomposites](#), *Advanced Materials*, **2021**, 1-7, 2107843. <https://doi.org/10.1002/adma.202107843>

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Controlling self-assembly of nanocomposites is a fundamental challenge with exciting implications for next-generation advanced functional materials. Precursors for composites can be generated photochemically, but limited insight in the underlying processes has hindered precise hands-on guidance. In this study, light-controlled nucleation and growth is demonstrated for self-assembling composites according to precise user-defined designs. Carbonate is generated photochemically with UV light to steer the precipitation of nanocomposites of barium carbonate nanocrystals and amorphous silica ($\text{BaCO}_3/\text{SiO}_2$). Using a custom-built optical setup, the self-assembly process is controlled by optimizing the photogeneration, diffusion, reaction, and precipitation of the carbonate species, using the radius and intensity of the UV-light irradiated area and reaction temperature. Exploiting this control, nucleation is induced and the contours and individual features of the growing composite are sculpted according to micrometer-defined light patterns. Moreover, moving light patterns are exploited to create a constant carbonate concentration at the growth front to draw lines of nanocomposites with constant width over millimeters with micrometer precision. Light-directed generation of local gradients opens previously unimaginable opportunities for guiding self-assembly into functional materials.

- A.V. Mader, L. Helmbrecht, W.L. Noorduin, [Multi-layered Barium and Strontium Carbonate Structures Induced by the Small Organic Dye Acid Orange 7](#), *Crystal Growth & Design*, **2021**, 21, 6349–6356. <https://doi.org/10.1021/acs.cgd.1c00823>

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The crystal growth behavior induced by small molecular additives is commonly assumed to be far less complex and rich in comparison to that obtained when using macromolecules. Herein, we demonstrate that the small organic molecule Acid Orange 7 can induce a large diversity of multi-layered barium carbonate structures. These multi-layered structures stem from the small molecule imperfectly blocking the fastest growing crystal face. By tuning the balance of growth and inhibition, we control the layer shape and thickness of the structures. Extending these strategies to strontium carbonate enables the precipitation of large quasi two-dimensional multi-layer sheets. Collectively, these findings highlight the unforeseen potential for using small organic molecules to induce the formation of complex inorganic structures.

- J. Jung, R.L.M. Op het Veld, R. Benoist, O.A.H. van der Molen, C. Manders, M.A. Verheijen, E.P.A.M. Bakkers, [Universal Platform for Scalable Semiconductor-Superconductor Nanowire Networks](#), *Advanced Functional Materials*, **2021**, 31, 2103062.
<https://doi.org/10.1002/adfm.202103062>

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Semiconductor-superconductor hybrids are commonly used in research on topological quantum computation. Traditionally, top-down approaches involving dry or wet etching are used to define the device geometry. These often aggressive processes risk causing damage to material surfaces, giving rise to scattering sites particularly problematic for quantum applications. Here, a method that maintains the flexibility and scalability of selective area grown nanowire networks while omitting the necessity of etching to create hybrid segments is proposed. Instead, it takes advantage of directional growth methods and uses bottom-up grown indium phosphide (InP) structures as shadowing objects to obtain selective metal deposition. The ability to lithographically define the position and area of these objects and to grow a predefined height ensures precise control of the shadowed region. The approach by growing indium antimonide nanowire networks with well-defined aluminium and lead (Pb) islands is demonstrated. Cross-section cuts of the nanowires reveal a sharp, oxide-free interface between semiconductor and superconductor. By growing InP structures on both sides of in-plane nanowires, a combination of platinum and Pb can independently be shadow deposited, enabling a scalable and reproducible in situ device fabrication. The semiconductor-superconductor nanostructures resulting from this approach are at the forefront of material development for Majorana based experiments.

- E. M. T. Fadaly, A. Marzegalli, Y. Ren; L. Sun; A. Dijkstra, D. De Matteis, E. Scalise; A. Sarikov; M. De Luca, R. Rurali, J.E.M. Haverkort, S. Botti, L. Miglio, E. P. A. M. Bakkers, M.A. Verheijen, [Unveiling Planar Defects in Hexagonal Group IV Materials](#). *Nano Letters* **21**(2021), No. 8, 3619-3625.
<https://doi.org/10.1021/acs.nanolett.1c00683>

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Recently synthesized hexagonal group IV materials are a promising platform to realize efficient light emission that is closely integrated with electronics. A high crystal quality is essential to assess the intrinsic electronic and optical properties of these materials unaffected by structural defects. Here, we

identify a previously unknown partial planar defect in materials with a type I_3 basal stacking fault and investigate its structural and electronic properties. Electron microscopy and atomistic modeling are used to reconstruct and visualize this stacking fault and its terminating dislocations in the crystal. From band structure calculations coupled to photoluminescence measurements, we conclude that the I_3 defect does not create states within the hex-Ge and hex-Si band gap. Therefore, the defect is not detrimental to the optoelectronic properties of the hex-SiGe materials family. Finally, highlighting the properties of this defect can be of great interest to the community of hex-III-Ns, where this defect is also present.

- Roberto Bergamaschini, Rianne C. Plantenga, Marco Albani, Emilio Scalise, Yizhen Ren, Håkon Ikaros T. Hauge, Sebastian Kölling, Francesco Montalenti, Erik P.A.M. Bakkers, Marcel A. Verheijen, Leo Miglio, [Prismatic Ge-rich inclusions in the hexagonal SiGe shell of GaP-Si-SiGe nanowires by controlled faceting](#), *Nanoscale*, **2021**, 13, 9436-9445
<https://doi.org/10.1039/D0NR08051A>

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Formation of Ge-rich prismatic inclusions in the hexagonal SiGe shell of GaP-Si-SiGe nanowires is reported and discussed in relation to a growth model that explains their origin. An accurate TEM/EDX analysis shows that such prisms develop right on top of any $\{11\bar{2}0\}$ facet present on the inner GaP-Si surface, with the base matching the whole facet extension, as large as tens of nanometers, and extending within the SiGe shell up to a thickness of comparable size. An enrichment in Ge by around 5% is recognized within such regions. A phase-field growth model, tackling both the morphological and compositional evolution of the SiGe shell during growth, is exploited to assess the mechanism behind the prism formation. A kinetic segregation process, stemming from the difference in surface mobility between Ge (faster) and Si (slower), is shown to take place, in combination with the evolution of the SiGe shell morphology. Actually, the latter moves from the one templated by the underlying GaP-Si core, including both $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ facets, to the more energetically convenient hexagon, bounded by $\{10\bar{1}0\}$ facets only. Simulations are shown to accurately reproduce the experimental observations for both regular and asymmetric nanowires. It is then discussed how a careful control of the GaP core faceting, as well as a proper modulation of the shell growth rate, allows for direct control of the appearance and size of the Ge-rich prisms. This tunability paves the way for a possible exploitation of these lower-gap regions for advanced designs of band-gap-engineering.

- K. Arts, H. Thepass, M.A. Verheijen, R.L. Puurunen, W.M.M. Kessels, H.C.M. Knoop, [Impact of Ions on Film Conformality and Crystallinity during Plasma-Assisted Atomic Layer Deposition of TiO₂](https://doi.org/10.1021/acs.chemmater.1c00781), *Chemistry of Materials*, **2021**, 33, 13, 5002-5009.
<https://doi.org/10.1021/acs.chemmater.1c00781>

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This work demonstrates that ions have a strong impact on the growth per cycle (GPC) and material properties during plasma-assisted atomic layer deposition (ALD) of TiO₂ (titanium dioxide), even under mild plasma conditions with low-energy (<20 eV) ions. Using vertical trench nanostructures and microscopic cavity structures that locally block the flux of ions, it is observed that the impact of (low-energy) ions is an important factor for the TiO₂ film conformality. Specifically, it is demonstrated that the GPC in terms of film thickness can increase by 20 to >200% under the influence of ions, which is correlated with an increase in film crystallinity and an associated strong reduction in the wet etch rate (in 30:1 buffered HF). The magnitude of the influence of ions is observed to depend on multiple parameters such as the deposition temperature, plasma exposure time, and ion energy, which may all be used to minimize or exploit this effect. For example, a relatively moderate influence of ions is observed at 200 °C when using short plasma steps and a grounded substrate, providing a low ion-energy dose of ~1 eV nm⁻² cycle⁻¹, while a high effect is obtained when using extended plasma exposures or substrate biasing (~100 eV nm⁻² cycle⁻¹). This work on TiO₂ shows that detailed insight into the role of ions during plasma ALD is essential for precisely controlling the film conformality, material properties, and process reproducibility.

- Hanglong Wu, Teng Li, Sai P. Maddala, Zafeiris J. Khalil, Rick R. M. Joosten, Brahim Mezari, Emiel J. M. Hensen, Gijbertus de With, Heiner Friedrich, Jeroen A. van Bokhoven, Joseph P. Patterson, [Studying Reaction Mechanisms in Solution Using a Distributed Electron Microscopy Method](https://doi.org/10.1021/acsnano.1c02461), *ACS Nano* **2021**, 15, 10296–10308.
<https://doi.org/10.1021/acsnano.1c02461>

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Electron microscopy (EM) of materials undergoing chemical reactions provides knowledge of the underlying mechanisms. However, the mechanisms are often complex and cannot be fully resolved using a single method. Here, we present a distributed electron microscopy method for studying

complex reactions. The method combines information from multiple stages of the reaction and from multiple EM methods, including liquid phase EM (LP-EM), cryogenic EM (cryo-EM), and cryo-electron tomography (cryo-ET). We demonstrate this method by studying the desilication mechanism of zeolite crystals. Collectively, our data reveal that the reaction proceeds via a two-step anisotropic etching process and that the defects in curved surfaces and between the subunits in the crystal control the desilication kinetics by directing mass transport.

- Mark M.J. van Rijt, Sjoerd W. Nooteboom, Arno van der Weijden, Willem L. Noorduin, Gijsbertus de With, [Stability-limited ion-exchange of calcium with zinc in biomimetic hydroxyapatite](#), *Materials & Design*, **2021**, 207, 109846.
<https://doi.org/10.1016/j.matdes.2021.109846>

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The exchange of Ca^{2+} ions in hydroxyapatite (HAp) with Zn^{2+} ions into Zn-HAp is of interest for applications ranging from bone tissue engineering to the use as a precursor in subsequent ion-exchange reactions. Previous studies, using direct synthesis, showed that ~ 20 mol% Zn^{2+} ions can be incorporated into HAp, before byproducts are observed. However, this is realized at the cost of a loss in crystallinity and control over crystal size and shape with increasing amounts of Zn^{2+} ion incorporation. In this work a simple post-synthetic ion-exchange strategy for the formation of Zn-HAp has been investigated. By merely exposing HAp to high concentrations of zinc nitrate in water, up to 22 mol% of the Ca^{2+} ions can be displaced by Zn^{2+} ions without any measured loss in crystallinity and preservation of crystallite size and shape. It was found that the incorporation of Zn^{2+} ions destabilizes the HAp crystals resulting in their gradual dissolution and reprecipitation. Consequently, promoting the exchange of Ca^{2+} with Zn^{2+} ions using increased reaction times, sonication and increased temperature results in an increased dissolution of HAp and precipitation of hopeite crystals, thereby preventing the formation of more zinc rich Zn-HAp.

- Giulia Mirabello, Matthew GoodSmith, Paul H. H. Bomans, Linus Stegbauer, Derk Joester, Gijsbertus de With, [Iron phosphate mediated magnetite synthesis: a bioinspired approach](#), *Chem. Sci.*, **2021**, 12, 9458.
<https://doi.org/10.1039/D0SC07079C>

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The biomineralization of intracellular magnetite in magnetotactic bacteria (MTB) is an area of active investigation. Previous work has provided evidence that magnetite biomineralization begins with the formation of an amorphous phosphate-rich ferric hydroxide precursor phase followed by the eventual formation of magnetite within specialized vesicles (magnetosomes) through redox chemical reactions. Although important progress has been made in elucidating the different steps and possible precursor phases involved in the biomineralization process, many questions still remain. Here, we present a

novel *in vitro* method to form magnetite directly from a mixed valence iron phosphate precursor, without the involvement of other known iron hydroxide precursors such as ferrihydrite. Our results corroborate the idea that phosphate containing phases likely play an iron storage role during magnetite biomineralization. Further, our results help elucidate the influence of phosphate ions on iron chemistry in groundwater and wastewater treatment.

- Bernette M. Oosterlaken, Mark M. J. van Rijt, Rick R. M. Joosten, Paul H. H. Bomans, Heiner Friedrich, and Gijsbertus de With, [Time-Resolved Cryo-TEM Study on the Formation of Iron Hydroxides in a Collagen Matrix](#), *ACS Biomater. Sci. Eng.* **2021**, 7, 3123–3131. <https://doi.org/10.1021/acsbiomaterials.1c00416>

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The mineralization of collagen via synthetic procedures has been extensively investigated for hydroxyapatite as well as for silica and calcium carbonate. From a fundamental point of view, it is interesting to investigate whether collagen could serve as a generic mineralization template for other minerals, like iron oxides. Here, bio-inspired coprecipitation reaction, generally leading to the formation of magnetite, is used to mineralize collagen with iron hydroxides. Platelet-shaped green rust crystals form outside the collagen matrix, while inside the collagen, nanoparticles with a size of 2.6 nm are formed, which are hypothesized to be iron (III) hydroxide. Mineralization with nanoparticles inside the collagen solely occurs in the presence of poly(aspartic acid) (pAsp). In the absence of pAsp, magnetite particles are formed around the collagen. Time-resolved cryo-TEM shows that during the coprecipitation reaction, initially a beam-sensitive phase is formed, possibly an Fe³⁺–pAsp complex. This beam-sensitive phase transforms into nanoparticles. In a later stage, sheet-like crystals are also found. After 48 h of mineralization, ordering of the nanoparticles around one of the collagen sub-bands (the a-band) is observed. This is very similar to the collagen–hydroxyapatite system, indicating that mineralization with iron hydroxides inside collagen is possible and proceeds via a similar mechanism as hydroxyapatite mineralization.

- Bernette M. Oosterlaken, Heiner Friedrich and Gijsbertus de With, [The effects of washing a collagen sample prior to TEM examination](#), *Microsc. Res. Tech.* **2022**, 85, 412–417. <https://doi.org/10.1002/jemt.23915>

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Transmission electron microscopy (TEM) is an important analysis technique to visualize (bio)macromolecules and their assemblies, including collagen fibers. Many protocols for TEM sample preparation of collagen involve one or more washing steps to remove excess salts from the dispersion that could hamper analysis when dried on a TEM grid. Such protocols are not standardized and

washing times as well as washing solvents vary from procedure to procedure, with each research group typically having their own protocol. Here, we investigate the influence of washing with water, ethanol, but also methanol and 2-propanol, for both mineralized and unmineralized collagen samples via a protocol based on centrifugation. Washing with water maintains the hydrated collagen structure and the characteristic banding pattern can be clearly observed. Conversely, washing with ethanol results in dehydration of the fibrils, often leading to aggregation of the fibers and a less obvious banding pattern, already within 1 min of ethanol exposure. As we show, this process is fully reversible. Similar observations were made for methanol and propanol. Based on these results, a standardized washing protocol for collagenous samples is proposed.

- Xufeng Xu, Baohu Wu, Helmut Cölfen, Gijsbertus de With, [Assembly Control at a Low Péclet Number in Ultracentrifugation for Uniformly Sized Nanoparticles](https://doi.org/10.1021/acs.jpcc.1c00143), *J. Phys. Chem. C* **2021**, 125, 8752–8758. <https://doi.org/10.1021/acs.jpcc.1c00143>

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The intrinsic high diffusion rate of colloids at low Péclet number results in an extremely fast crystallization process and instant formation of colloidal crystals, even at an ultracentrifugal field of extremely high intensity. By introducing a small number of clusters in sedimentation, it should be possible to slow down the crystallization process, thus making the assembly order tunable in preparative ultracentrifugation experiments. Here, we used sodium dodecyl sulfate-stabilized polystyrene nanoparticles (with a size dispersity of 1.07) dispersed in a solution of high ionic strength. Sedimentation and assembly of these nanoparticles were done using preparative ultracentrifugation at various angular velocities. The sedimentation process was also analyzed in situ by analytical ultracentrifugation in real time. By creating as low as 3% of clusters into these nearly uniformly sized polystyrene nanoparticle dispersions during the sedimentation process, the superstructure order becomes easily tunable between glassy and crystalline. Theoretical calculations complemented the experiments to explain the mechanism of cluster formation in sedimentation. This work provides a novel methodology to produce superstructures with a tunable packing order for colloids at low Péclet number.

- E. Deniz Eren, Wouter H. Nijhuis, Freek van der Weel, Aysegul Dede Eren, Sana Ansari, Paul H.H. Bomans, Heiner Friedrich, Ralph J. Sakkers, Harrie Weinans, Gijsbertus de With, [Multiscale characterization of pathological bone tissue](#), *Microsc. Res. Tech.* **2022**, 85, 469–486.
<https://doi.org/10.1002/jemt.23920>

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Bone is a complex natural material with a complex hierarchical multiscale organization, crucial to perform its functions. Ultrastructural analysis of bone is crucial for our understanding of cell to cell communication, the healthy or pathological composition of bone tissue, and its three-dimensional (3D) organization. A variety of techniques has been used to analyze bone tissue. This article describes a combined approach of optical, scanning electron, and transmission electron microscopy for the ultrastructural analysis of bone from the nanoscale to the macroscale, as illustrated by two pathological bone tissues. By following a top-down approach to investigate the multiscale organization of pathological bones, quantitative estimates were made in terms of calcium content, nearest neighbor distances of osteocytes, canaliculi diameter, ordering, and D-spacing of the collagen fibrils, and the orientation of intrafibrillar minerals which enable us to observe the fine structural details. We identify and discuss a series of two-dimensional (2D) and 3D imaging techniques that can be used to characterize bone tissue. By doing so we demonstrate that, while 2D imaging techniques provide comparable information from pathological bone tissues, significantly different structural details are observed upon analyzing the pathological bone tissues in 3D. Finally, particular attention is paid to sample preparation for and quantitative processing of data from electron microscopic analysis.

- J. J. Devogelaer, M. D. Charpentier, A. Tijink, V. Dupray, G. Coquerel, K. Johnston, H. Meekes, P. Tinnemans, E. Vlieg, J. H. ter Horst, R. de Gelder. [Cocrystals of praziquantel: Discovery by network-based link prediction](https://doi.org/10.1021/acs.cgd.1c00211), *Cryst. Growth & Des.*, **21** (2021) 3428-3437. <https://doi.org/10.1021/acs.cgd.1c00211>

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Cocrystallization has been promoted as an attractive early development tool as it can change the physicochemical properties of a target compound and possibly enable the purification of single enantiomers from racemic compounds. In general, the identification of adequate cocrystallization candidates (or cofomers) is troublesome and hampers the exploration of the solid-state landscape. For this reason, several computational tools have been introduced over the last two decades. In this study, cocrystals of Praziquantel (PZQ), an anthelmintic drug used to treat schistosomiasis, are predicted with network-based link prediction and experimentally explored. Single crystals of 12 experimental cocrystal indications were grown and subjected to a structural analysis with single-crystal X-ray diffraction. This case study illustrates the power of the link-prediction approach and its ability to suggest a diverse set of new cofomer candidates for a target compound when starting from only a limited number of known cocrystals.

- R. Aninat, F.J. van den Bruele, J.J. Schermer, P. Tinnemans, J. Emmelkamp, E. Vlieg, M. van der Vleuten, H. Linden, M. Theelen, [In-situ XRD study on the selenisation parameters driving Ga/In interdiffusion in Cu\(In,Ga\)Se₂ in a versatile, industrially-relevant selenisation furnace](https://doi.org/10.1016/j.solener.2021.11.032), *Solar Energy* **230** (2021) 1085-1094. <https://doi.org/10.1016/j.solener.2021.11.032>

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The selenisation of Cu-Ga-In metallic precursors is investigated by in-situ X-Ray Diffraction (XRD) in a selenisation tool which mimics at the laboratory scale an industrial tool (thus fully scalable) and allows fine control over the selenisation parameters and reproducibility. In this setup, the interdiffusion of Ga and In was significantly accelerated by decreasing the Se crucible temperature or increasing the sample temperature. Applying a lower Se crucible temperature yielded a very fast initial interdiffusion that quickly reached a steady-state, non-flat Ga/(Ga + In) (GGI) depth profile. On the other hand, the higher crucible temperature tested led to a slower interdiffusion which kept evolving to a flatter GGI profile after a sufficiently long dwell time at the maximum temperature. Strategies to gain better control over the GGI profile, and hence bandgap profile, are discussed. The results indicate that the versatility of the setup is key to achieving fine control over the GGI depth profile, which is particularly relevant today, when new alkali doping strategies are being introduced.

- Daan van der Woude, Luc van der Krabben, Gerard Bauhuis, Maarten van Eerden, Jae Jin Kim, Peter Mulder, Joost Smits, Elias Vlieg and John Schermer, [Ultrathin GaAs solar cells with a high surface roughness GaP layer for light-trapping application](https://doi.org/10.1002/pip.3534), *Progress in Photovoltaics: Research and Application*, <https://doi.org/10.1002/pip.3534>

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By reducing the thickness of the absorber layers, ultrathin GaAs solar cells can be fabricated in a more cost-effective manner using less source material and shorter deposition times. In this work, ultrathin GaAs solar cells are presented with a diffuse scattering layer based on wide bandgap GaP grown directly on the device layers of the cells with MOCVD. The roughness and surface morphology are quantified using atomic force microscopy and the resulting diffuse scattering capability is assessed using wavelength-dependent reflectance measurements. Ohmic rear contacts are made using contact points etched through the GaP layer, for which an etching procedure using I₂:KI was developed and optimized. The performance of the GaP textured ultrathin GaAs cells are compared with equivalent planar cells using current density-voltage measurements and external quantum efficiency measurements, where the GaP textured cells demonstrate an increase of 6.7% in the short-circuit current density (JSC), which was found to be as high as 21.9 mA·cm⁻² as a result of increased photon absorption by light-trapping.

- G. Belletti, J. Schuurman, H. Stinesen, H. Meeks, F. P.J.T. Rutjes, E. Vlieg, [Combining Viedma ripening and temperature cycling deracemization](https://doi.org/10.1021/acs.cgd.1c01423), *Cryst. Growth & Des.*, 22, 3, 1874–1881. <https://doi.org/10.1021/acs.cgd.1c01423>

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While much data are available for the Viedma ripening and temperature cycling deracemization processes, not much is known about the advantages (or disadvantages) of a combination of the two. We here try to elucidate what happens when Viedma ripening is used in combination with temperature cycling by comparing not only the deracemization times but also the change in the sizes of the crystals. We found that, in the case of NMPA (rac-(2-methylbenzylidene)-phenylglycine amide) as a model compound, combined experiments significantly increase the deracemization time. By tuning the process parameters, it is possible to approach experimental conditions where both Viedma ripening and temperature cycling control the deracemization. Under those conditions, however, the deracemization time is not significantly improved. Following our results, it seems unlikely that a combination of Viedma ripening and temperature cycling would shorten the deracemization time. Nevertheless, these experiments might provide clues for unraveling the mechanism of temperature cycling.

- T. Lerdwiriyanupap, G. Belletti, P. Tinnemans, H. Meekes, F. Rutjes, E. Vlieg, A. Flood, [Combining diastereomeric resolution and Viedma ripening using a racemic resolving agent](#), *Eur. J. Org. Chem.*, **2021** (2021), 5975–5980.
<https://doi.org/10.1002/ejoc.202101193>

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In spite of the many resolution techniques available to separate enantiomers, diastereomeric resolution still remains the most widely used technique in industry. However, drawbacks of this technique are the limited yield of the desired enantiomer and the expensive enantiopure resolving agent that is required. We show here for the first time that a combination of diastereomeric resolution with Viedma ripening using a racemic resolving agent can also provide a single stereoisomer when using an excess of the racemic resolving agent, without the need for the resolving agent to racemize. The requirements of this process are, like for an enantiomeric system, that the compound crystallizes as a racemic conglomerate and that at least one chiral center in the target molecule is racemizable. In addition, owing to the presence of the racemization reaction, substantial improvement in the yield can be obtained. We here demonstrate this approach using a metastable conglomerate salt of rac-2-phenylglycinamide with rac-N-acetyl tryptophan.

- F. Ibis, T. Wang Yu, F. Marques Penha, D. Ganguly, M. A. Nuhu, A. E. D. M. van der Heijden, H. J. M. Kramer and H. B. Eral, [Nucleation kinetics of calcium oxalate monohydrate as a function of pH, magnesium, and osteopontin concentration quantified with droplet microfluidics](#), *Biomicrofluidics*, **2021**, *15*, 064103.
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A droplet-based microfluidic platform is presented to study the nucleation kinetics of calcium oxalate monohydrate (COM), the most common constituent of kidney stones, while carefully monitoring the pseudo-polymorphic transitions. The precipitation kinetics of COM is studied as a function of supersaturation and pH as well as in the presence of inhibitors of stone formation, magnesium ions (Mg^{2+}), and osteopontin (OPN). We rationalize the trends observed in the measured nucleation rates leveraging a solution chemistry model validated using isothermal solubility measurements. In equimolar calcium and oxalate ion concentrations with different buffer solutions, dramatically slower kinetics is observed at pH 6.0 compared to pHs 3.6 and 8.6. The addition of both Mg^{2+} and OPN to the solution slows down kinetics appreciably. Interestingly, complete nucleation inhibition is observed at significantly lower OPN, namely, 3.2×10^{-8} M, than Mg^{2+} concentrations, 0.875×10^{-4} M. The observed inhibition effect of OPN emphasizes the often-overlooked role of macromolecules on COM nucleation due to their low concentration presence in urine. Moreover, analysis of growth rates calculated from

observed lag times suggests that inhibition in the presence of Mg^{2+} cannot be explained solely on altered supersaturation. The presented study highlights the potential of microfluidics in overcoming a major challenge in nephrolithiasis research, the overwhelming physiochemical complexity of urine.

PhD theses

- Mark M.J. van Rijt, Connecting ZnO to Organic Templates
PhD defense: 8 June 2021, Eindhoven University of Technology, Eindhoven

Promotor: Prof. Dr. G. de With

Co-promotor: Dr. H. Friedrich



In materials science there is a continuous strive to obtain materials with enhanced properties without introducing unwanted limitations. Inspiration for these materials can be found in nature, where the extraordinary control of biological processes results in excellent material properties, for example the impressive mechanical properties of bone, the surprising magnetic particles in magnetotactic bacteria and the beautiful iridescent colors of nacre shells. Many of these natural materials possess these properties due to a hybrid composition containing both organic and inorganic (mineral) phases. While nature has limited its choice to a few minerals, mainly silica, phosphates and carbonates, this is not the case for man-made materials. Therefore, by understanding and emulating the formation of natural materials with non-naturally incorporated minerals, a near endless range of new materials should be obtainable. An excellent candidate for this is the well-known metal oxide zinc oxide (ZnO). Its most common polymorph wurtzite ZnO has a wide range of relevant physical properties making it a material of interest for a multitude of technological applications including piezo-electrics, photocatalysis and solar cells. Mineralization of organic templates with ZnO should therefore allow for the expression and control over a wide range of material properties.

- Annemerel R. Mol, [Biocrystallization for elemental sulfur recovery](#)
PhD defense: 25 February 2022, Wageningen University & Research (WUR), Wageningen

Promotor: Prof dr ir C.J.N. Buisman

Co-promotores: Dr R.D. van der Weijden and Ir J.B.M. Klok

This thesis studied a biotechnological process in which naturally occurring microorganisms, let's call them 'desulfurizers', convert toxic and corrosive hydrogen sulfide (H₂S) gas to solid, reusable, and easily recoverable elemental sulfur crystals. H₂S needs to be removed from (bio)gas to prevent sulfur dioxide formation during combustion to avoid the formation of acid rain. By studying the biocrystallization mechanism of biologically formed sulfur, the settleability of the formed crystals was improved. A simple solution was discovered to do so: portion of the H₂S is used to partially dissolve the elemental sulfur crystals. In this process, a soluble sulfur component is formed: polysulfide. Polysulfide formation, and subsequent conversion back to elemental sulfur makes the crystals more prone to agglomeration, which improves their recovery efficiency. The recovered sulfur has many applications, such as reuse in agriculture as fertilizer or fungicide, but also is suitable to apply in industrial processes.

