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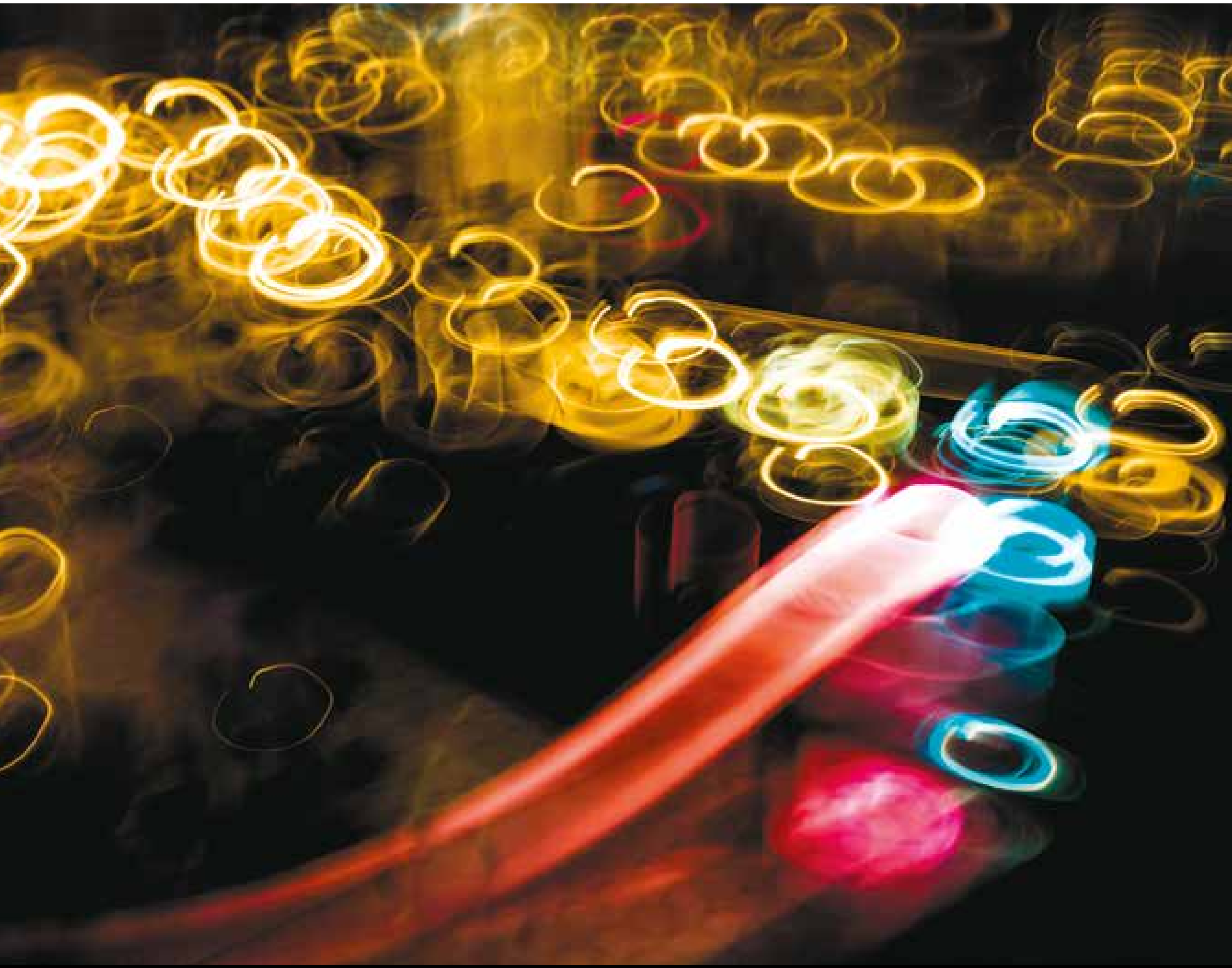
Debye Institute
for Nanomaterials Science



Postgraduate Research Projects 2021

Debye Institute
for Nanomaterials Science

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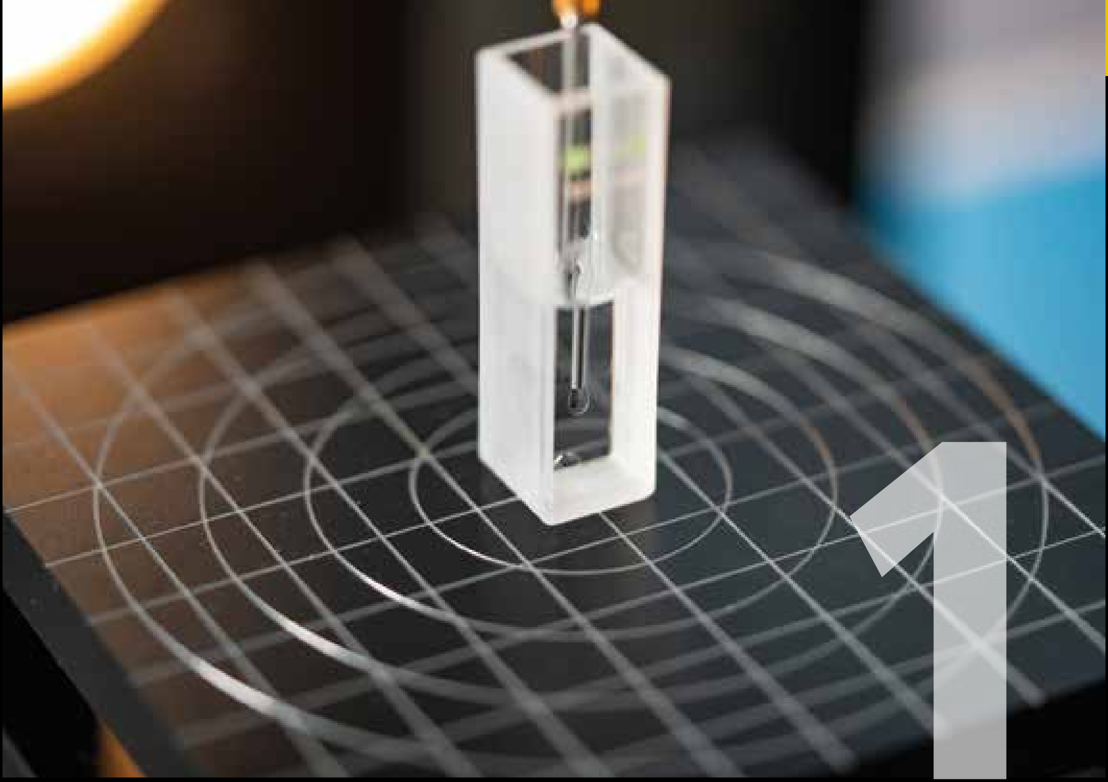
7-21

Contents



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Preface Debye Booklet

In this booklet, you will find an overview of the postgraduate research projects currently undertaken by PhD candidates and postdocs working in the various groups of the Debye Institute for Nanomaterials Science of Utrecht University. This booklet is intended to serve not only as an interesting overview of the scientific work to which the Debye Institute is associated, but also as an easy means with which to encourage collaboration between the different groups of the Debye Institute.

Each contribution consists of a brief summary of the work performed, with the most important aspects of the research project highlighted in the header. At the back of the booklet, you will find both the author index and the technique index. The author index lists all names of the PhD candidates and postdocs of the Debye Institute, and the technique index summarises the most commonly used spectroscopic and experimental techniques used by each research group, including the name and contact details of the member of staff responsible for each piece of equipment. Feel free to contact these persons if you are interested in performing a measurement in a different research group.

This book has been composed by the members of the Debye PhD Committee (Debye AiO Commissie, DAC), which is a representative body for the PhD candidates and postdocs of the institute. This year's edition of the Debye Booklet contains contributions for 165 postgraduate research projects. Especially, during the corona pandemic it was hard to connect and meet colleagues from other research groups. Therefore, the booklet is now an even more helpful tool to encourage collaborations. Welcome to the Debye Institute and good luck with your research!

On behalf of the DAC,
Suzan Schoemaker

Debye Institute for Nanomaterials Sciences

Welcome to the Debye Institute for Nanomaterials Science!
The Debye Institute was founded in 1989 with the aim to promote cooperation between chemists and physicists of Utrecht University in the areas of solids, surfaces, and interfaces. The institute is named in honour of a prominent Dutch scientist, Nobel Laureate, and Professor at Utrecht University, Peter Debye (1884-1966), whose contributions to the study of molecular structure embody the strength that chemical and physical research hold when performed in an interdisciplinary and collaborative manner.

Deemed world-leading by an international review committee in 2017, both in quality and relevance, our research involves three research lines: catalysis, colloids and nanophotonics. With the central research theme being "Nanomaterials for Sustainability", the institute brings together seven research groups from the departments of Chemistry and Physics:

- Condensed Matter and Interfaces
- Materials Chemistry and Catalysis
- Inorganic Chemistry and Catalysis
- Nanophotonics
- Organic Chemistry and Catalysis
- Soft Condensed Matter and Biophysics
- Van 't Hoff Laboratory for Physical and Colloid Chemistry

The individual research missions as well as the postgraduate research projects of each group will be presented in greater detail in the next sections of this booklet. Overall, the Debye Institute currently hosts about 165 PhD candidates and postdocs on a continuous basis.

Since the path forward towards a more sustainable future involves fundamental science on nanomaterials to a very significant extent, the future of the Debye Institute looks bright, and continues to receive support from Utrecht University, the Faculty of Science, the Department of Chemistry and the Department of Physics. More information about the Debye Institute for Nanomaterials Science can be found on the website: www.debye.uu.nl.

Debye Board Members

The board of the Debye Institute for Nanomaterials Science consists of prof. dr. Alard Mosk (scientific director), prof. dr. Petra de Jongh (vice-director), dr. Ingmar Swart (managing director) and prof. dr. ir. Marjolein Dijkstra and dr. Florian Meirer.

Scientific director	prof. dr. Alard Mosk	a.p.mosk@uu.nl
Vice director	prof. dr. Petra de Jongh	p.e.dejongh@uu.nl
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Management coordinator	Mirna Marrink	m.marrink@uu.nl
Secretary	Linda Kumeling	science.debye@uu.nl

The Debye PhD Committee

The Debye PhD Committee (Debye AiO Commissie, DAC) exists in order to represent the interest of all the different researchers currently working within the Debye Institute. Each research group is represented by at least one PhD candidate. Together, the DAC unites the various research groups by organising activities like the Debye Sports Day at the beginning of each academic year and the social events during the Debye Spring School. The DAC also contributes to the educational programme by organising the biannual career-oriented Debye DO! Days event, where PhD candidates have the chance to discuss future career moves with employees across a broad scope of science-orientated jobs. If you have any questions regarding the DAC, the Debye Institute, or any upcoming events, please do not hesitate to contact the DAC representative of your group. A list of the current DAC members is provided below:

Group	Representative	E-mail
Condensed Matter and Interfaces	Rian Ligthart	r.a.m.ligthart@uu.nl
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Soft Condensed Matter & Biophysics	Marjolein de Jager	m.e.dejager@uu.nl
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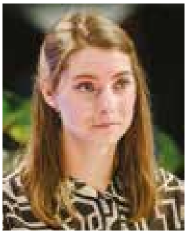
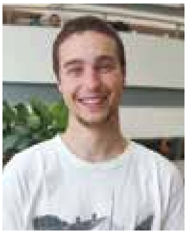


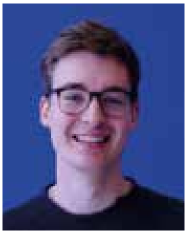
Suzan (MCC)

James (PCC)

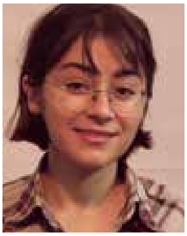


Luke (OCC)

Marjolein (SCMB)



Mark (SCMB)



Pegah (NP)

Rian (CMI)

Sebastian (ICC)

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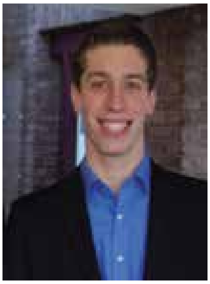
CONDENSED MATTER AND INTERFACES

Scientific staff	prof. dr. Andries Meijerink, prof. dr. Daniël Vanmaekelbergh, dr. Celso de Mello Donegá, dr. Ingmar Swart, dr. Zeila Zanolli
Adjunct staff	prof. dr. John Kelly, prof. dr. Harold de Wijn, dr. Onno Gijzeman
Technical support	Peter van den Beld, Stephan Zevenhuizen
Administrative staff	Linda Kumeling, Silvia Benschop
PhD students/Postdocs	20

Research Mission

The research of the CMI group is focused on the synthesis of nanostructured opto-electronic materials and characterizing and understanding their structural, optical and electrical properties. There is a strong link with applications of these materials in photovoltaics, lighting and medical imaging. We aim to relate the local microscopic structure and properties measured on the nanoscale with the overall opto-electronic properties of the material thus providing a deeper fundamental understanding.

Investigating Majorana fermions with shot-noise STM



Jan Cuperus, j.p.cuperus@uu.nl
Sponsor: ERC, since September 2020
Supervisors: dr. Ingmar Swart, prof. dr. Daniël Vanmaekelbergh

Majorana zero modes, Shot-noise measurements, Scanning Tunneling Microscopy

In the field of condensed matter, there is a broad interest in topological materials. In such materials, certain electronic states are protected from local defects. This makes these states robust and possible candidates for next-gen electronic applications. Majorana bound states are an example of topological states. These states can be seen as a type of quasiparticle: Majorana fermions. Majorana fermions possess the exotic properties to (1) be their own antiparticle and (2) obey non-Abelian statistics. This last property may open the path towards topological quantum computing.

There are several publications reporting the observation of Majorana fermions in atomic chains that are in the proximity of a superconductor. However, none of these reports are conclusive; the observations could be explained by alternative reasonings. In my research, we hope to shed some light on the existence of Majorana particles by using two techniques: atom manipulation and shot-noise measurements.

Both these techniques will be combined within framework of scanning tunneling microscopy (STM). Using a STM, the surfaces of semi-, normal and superconductors can be investigated both physically and electronically. Moreover, the extreme resolution of the STM (sub-pm) can be used to alter the structure of a surface atom-by-atom. We would like to use that ability to create atomic structures (e.g. chains) in proximity to a superconductor. Subsequently, we would like to perform shot-noise spectroscopy measurements on these chains. Such measurements are predicted to be able to distinguish Majorana fermions from other, similar (quasi)particles. To be able to perform shot-noise measurements with atomic precision, requires the use of a specially designed MHz preamplifier[1], which will be installed in our new 300 mK STM.

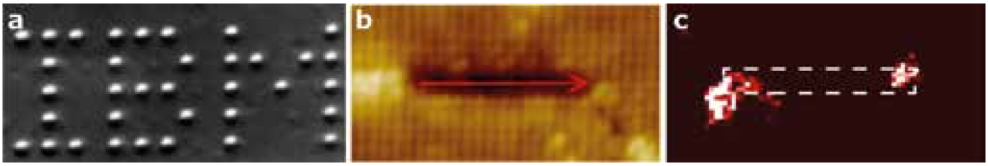


Figure 1: a) 35 Xe atoms arranged one by one to form the letters IBM.[2] b) Atomic line defect in the surface of Fe(Te, Se) hosting the states shown in c). c) dI/dV mapping of the line defect showing the presence of what might be a pair of Majorana particles. [3]

[1] K. M. Bastiaans, T.Benschop, D. Chatzopoulos, *et al.*, *Rev. Sci. Instrum* **89**, 093709 (2018)
[2] D. M. Eigler, E. K. Schweizer, *Nature* **344**, 524-526 (1990)
[3] C. Chen, K. Jiang, K., Y. Zhang, *et al.*, *Nat. Phys.* **16**, 536-540 (2020)

Synthesis and characterization of colloidal topological (crystalline) insulators

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Sponsor: ERC grant, since October 2020
Supervisors: prof. dr. Daniël Vanmaekelbergh, dr. Ingmar Swart

Topological (crystalline) insulators, Colloidal nanomaterials, Scanning Tunneling Microscopy/Spectroscopy

Topological insulators (TIs) have gained much interest in condensed matter physics due to their unique electronic properties. These materials are characterized by an insulating bulk with topologically protected metallic quantum states at their surface (3D materials) or edge (2D materials). This protection is related to the inversion of the conduction and valence band as a consequence of strong spin-orbit coupling, which results in robust surface states that remain metallic despite the presence of disorder or impurities. The robust surface, combined with exotic effects such as spin-filtering, have resulted in TIs being regarded as highly intriguing materials for material science, nanoelectronics, and spintronics.[1]

Of the verified TIs, Bi_2Se_3 serves as a model system due to its large inverted bulk bandgap (0.3 eV) and its helical edge state, which manifests as a Dirac cone situated at the Γ point in the Brillouin zone.[2] While extended sheets and bulk crystals of Bi_2Se_3 have been investigated with scanning tunnelling microscopy (STM) and spectroscopy (STS), reports on the electronic properties of Bi_2Se_3 nanoplatelets (NPLs) are scarce.[3] However, the small lateral size of NPLs and their specific crystal structure provide a unique opportunity to study the effects of quantum confinement and shape on the NPLs' opto-electronic properties. We therefore aim to synthesize colloidal Bi_2Se_3 NPLs and investigate their properties with STM/STS as shown in figure 1a.
In addition to investigating Bi_2Se_3 NPLs, our goal is to prepare and characterize colloidal topological crystalline insulators (TCIs) of SnTe, $Pb_{1-x}Sn_xSe$, and $Pb_{1-x}Sn_xTe$ (see figure 1b). Such TCIs constitute a subclass of TIs in which the surface states are protected by the point group symmetry of the crystal. We are currently developing a synthesis route using cation exchange and one-pot synthesis techniques to obtain SnTe NPLs and nanocrystals of $Pb_{1-x}Sn_xSe$ and $Pb_{1-x}Sn_xTe$ with tunable dimensions and composition.

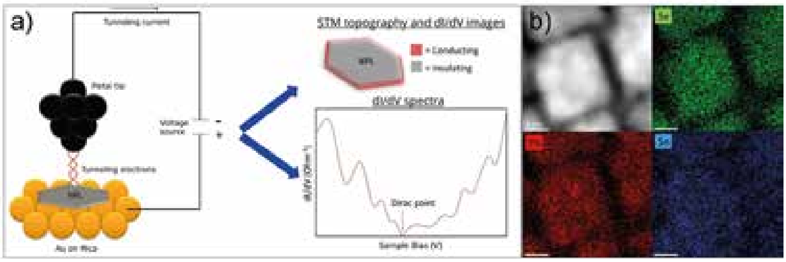

Figure 1: a) Graphical representation of the STM set-up and the types of results that can be obtained. b) HAADF-STEM image and STEM-EDX element maps of $Pb_{1-x}Sn_xSe$ nanocubes, showing a homogeneous distribution of Pb and Sn in the particles. Scale bars are 5 nm.

[1] Ramirez, Arthur P., and Skinner, Brian, *Nat. Phys.* **73**, 30-36 (2020)
[2] Zhang, Yi *et al.*, *Nat. Phys.* **6**, 584-588 (2010)
[3] Bhunia, Hrishikesh *et al.*, *Phys. Chem. Chem. Phys.* **19**, 9872-9878 (2017)

The wide world of STM

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Sponsor:	NWO, since February 2019
Supervisors:	prof. dr. Daniël Vanmaekelbergh, dr. Ingmar Swart

Scanning Tunnelling Microscopy, Spin-Orbit Coupling, Magnetic field measurements

Over the years the condensed matter and interfaces group at Utrecht University has had a wide array of scientific interests. This has led to many collaborations both internally and with researchers from other universities. My research also shows this as I am focussed on many different topics collaborating with many different researchers.

The common denominator is the Scanning Tunnelling Microscope (STM). This microscope uses Tunnelling electrons to probe metallic substrates. Using this technique it is possible to image individual atoms, probe electronic structures and position individual particles in specific locations. The first focus of my research has been to create artificial lattices of lead (Pb) adatoms on a Cu(111) substrate. Previous work in the group has showed that lattices of CO on Cu(111) can give insight of the electronic properties of material which can't be found in nature (yet).[1] By changing the CO for Pb adparticles we introduce spin-orbit coupling into the system which can have interesting features. The next project involves nanoparticles synthesized by researcher in our group. These particles exhibit interesting electronic properties due to their size and crystalline structure such as Topological edge states and the Aharanov Bohm effect.[2] Lastly a cooperation with the TU in Eindhoven has given us the opportunity to examine Molecular Beam Epitaxial grown samples of semiconductor materials such as GaAs. Our joined project focuses on the dopants in these samples and how they react to a magnetic field. In theory the magnetic field changes the conductance through these dopants, which can be investigated by hovering the tip of the STM over the dopants and measuring the conductance while ramping a magnetic field.[3]

[1] Gardenier T S *et al.*, *ACS Nano* **14**, 13638 (2020)

[2] Bhunia H *et al.*, *Phys. Chem. Chem. Phys.* **19**, 9872 (2017)

[3] McMillan S R *et al.*, *Phys. Rev. Lett.* **125**, 257203 (2020)

Synthesis and characterization of red-emitting phosphors

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Sponsor: TKI, since August 2019
Supervisors: prof. dr. Andries Meijerink, dr. Freddy Rabouw
Lanthanide luminescence, Energy transfer, Nanocrystal synthesis

LEDs are currently the most efficient form of lighting available for many applications. Typically, a blue-emitting LED is covered with a phosphor layer, which absorbs part of the blue light and converts this into other colors, together forming white light. Phosphors therefore play an important role in the efficiency and color gamut of displays and consumer lighting. Currently, there are two major challenges in the LED industry that need to be addressed for red phosphors: efficient blue LED sensitization of Eu^{3+} and the occurrence of phosphor saturation at high LED powers. Our goal is to find materials that can alleviate these problems and understand how these processes work.

Most widely used red-emitting phosphors have part of their emission spectrum is in the near infrared. Therefore, an interesting alternative ion is Eu^{3+} due to its narrow red emission bands around 615 nm, where the eye sensitivity is high. The challenge with Eu^{3+} is its very weak absorption in the blue because of strongly forbidden f-f transitions. A promising method to overcome the weak absorption of Eu^{3+} is to use strongly absorbing semiconductor nanocrystals (NC) that transfer their energy to incorporated Eu^{3+} ions.[1] In recent years elpasolite NCs emerged as an interesting class of semiconductor materials for lanthanide incorporation. By changing the materials composition, optoelectronic properties such as absorption and emission wavelength can be tuned. More importantly it has a octahedral (CN=6) position occupied by a trivalent metal, which makes it an interesting candidate for lanthanide substitution. My goal is to synthesize and analyze stable elpasolite NC compositions that facilitate efficient energy transfer from the absorbing host material to the Eu^{3+} ion.

The second part of my research focuses on phosphor saturation at high luminescence intensity. Typical blue LEDs operate at temperatures up to 120°C and give rise to blue luminescence of around 2 W/mm^2, at which intensities several efficiency limiting processes can take place.[2] For example, K_2SiF_4 doped with Mn^{4+} is well-known for its applications in display technologies, but has found limited applications in consumer lighting due to phosphor saturation and thermal quenching effects. Based on careful measurements at varying intensities and temperatures we try to understand and alleviate these effects for common red phosphors.

[1] Marin *et al.*, *Chem. Rev.*, 1425-1462 (2020)
[2] van de Haar *et al.*, *ACS photonics*, 1784–1793 (2021)

Synthesis and characterization of two dimensional nanocrystal superlattices

Maaike van der Sluijs, m.m.vandersluijs@uu.nl
Sponsor: ERC, since November 2017
Supervisors: prof. dr. Daniel Vanmaekelbergh

Synthesis, Self-assembly, Oriented attachment

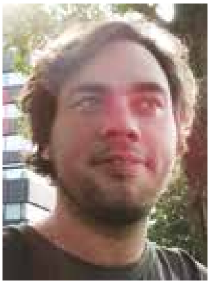
Superlattices of nanocrystals are interesting for numerous applications, ranging from solar cells to LEDs. These systems have properties that depend both on the particles from which they are formed and on the structure of the superlattice. Graphene for instance, has interesting electronic properties due to its honeycomb structure, such as Dirac cones with massless charge carriers. Tight-binding calculations have shown that semiconductors in a honeycomb structure are likely to have a similar high carrier mobility as graphene, but with the added benefit of an optical band gap.[1,2]

Previously, it has been shown that lead chalcogenide nanocrystals can form superlattices with a square or a honeycomb structure.[3] A dilute dispersion of the nanocrystals is drop-casted on an immiscible liquid substrate, where the solvent slowly evaporates causing the nanocrystals to self-assemble. The nanocrystals attach to each other via specific facets, a process called oriented attachment, to form 2D superlattices. The formation of square superlattices from PbSe nanocrystals has been elucidated with transmission electron microscopy (TEM), in-situ grazing incidence small-angle and wide angle X-ray scattering (GISAXS/WAXS).[4]

Despite these promising advances, there are still many unanswered questions in this field. An important aspect of this project is to improve the reproducibility of the superlattices and to optimize them. These improved superlattices will allow us to access superlattices with different compositions via cation exchange, while surface passivation will improve the stability of the superlattices for electrochemical and structural characterisation. These findings form the basis for the study of the adsorption geometry of the nanocrystals at the liquid/air interface and the elucidation of the formation mechanism of the honeycomb superlattice.

[1] E. Kalesaki *et al.*, *Phys. Rev. B*, **88**, 115431 (2013)
[2] E. Kalesaki *et al.*, *Phys. Rev. X*, **4**, 011010 (2014)
[3] W. H. Evers *et al.*, *Nano Lett.* **13**, 2317-2323 (2013)
[4] J. J. Geuchies *et al.*, *Nat. Mater.* **15**, 1248-1254 (2016)

Narrowband green and narrowband red emitters for LED applications



Naud van Bunningen, A.j.vanbunningen@uu.nl
Sponsor: NICHIA, September 2018
Supervisors: prof. Dr. Andries Meijerink

Transition metal luminescence, Energy transfer

As the world is getting more aware of its environmental impact, the need for efficient electric devices is a necessity. Light emitting diodes (LEDs) are a good example of efficient and environmental friendly candidate to replace current tube lighting or the even worse incandescent lighting. Although LEDs are extremely efficient to their predecessor, LEDs can still be improved: the lumens (light that we can perceive) per watt for the green and especially the red light can be improved. The green phosphor can still be improved to optimize the colour quality. It was hypothesized that Manganese can be a suitable candidate to enhance the phosphors in modern day LEDs.

In my research, I focus on the manganese ion Mn^{2+}. Typically Mn is doped in host matrices with a strong ionic character. In my research I study how the surrounding host matrix determines the luminescence properties of the Mn^{2+}. This is done by synthesizing various ionic structures, doping these with various concentrations of Mn^{2+}. The synthesis is typically done by mixing oxide precursors and mixing them thoroughly before putting them in a high temperature oven (800-1800C). Firstly the phase purity is checked by powder X-ray diffraction. Afterwards photo luminescent spectra and decay curves are measured. In addition, all these measurements can be done at cryogenic temperatures as well at elevated temperatures. The combination of different host matrixes and the various spectroscopic measurements leads to a proper understanding of how the local structure around the Mn^{2+} determines its optical properties. In addition thermal stimulated luminescence spectra can be done to study the filling and emptying of so called 'traps' in the host matrix.

By understanding the structure dependent phenomena better we can aid the engineers in their search for new promising phosphors for LEDs.

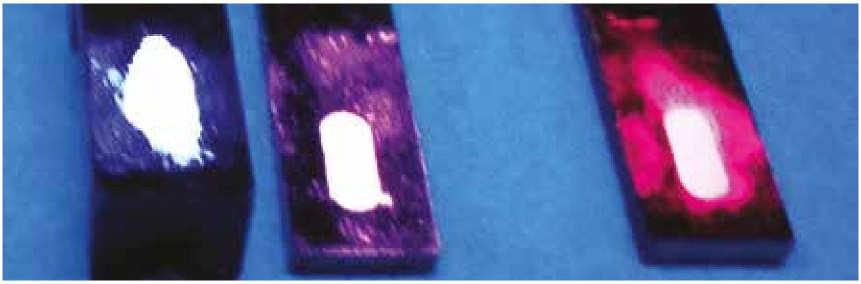


Figure 1: Three $Ca_3(PO_4)_2$:Eu/Mn samples under 254nm synthesized under varying conditions

Topological excitonics

Pedro Miguel M. C. de Melo, p.m.monteirocamposdemelo@uu.nl
Sponsor: Sector plan 2019 - 2024, since October 2020
Supervisors: dr. Zeila Zanolli, prof. dr. ir. Henk Stoof
Optical properties, Topological Insulators, Excitons

Topological insulators (TIs) differ from traditional semiconductors due to the presence of protected conducting surface states, which offer the possibility of dissipationless scattering.[1,2] This is due to a combination of time-reversal symmetry and spin-orbit coupling. While electronic TIs have been extensively studied both theoretically and experimentally, the possibility of extending this concept to quasiparticles constituted by bound electron-hole states (excitons) has barely been explored. Recently it was shown that the electronic topological features can be transferred to excitons in Bi_2Se_3, a prototypical TI, using a single-particle model Hamiltonian on top of k.p theory.[3] This important first step was however based on effective 2D parameters, and is valid for intermediate and implicit film thicknesses. But, being dependent on the particular symmetries of the material, it cannot be immediately generalised to other TIs.

For the first time, we investigate the optical properties of excitons in Bi_2Se_3, a prototypical TI, using many-body first-principles methods with the Yambo[4] package. We discuss the evolution of electronic and optical properties from bulk to few-layer systems and their connection to surface states. We define and implement a new topological invariant for excitons, to classify their topological behavior from bulk to monolayers, and demonstrate under which conditions the excitons inherit the topological character of the electrons and holes that constitute them. This knowledge will be instrumental in future work on topological excitons, in particular to deal with the interaction between a TI and a (pulsed) laser field.

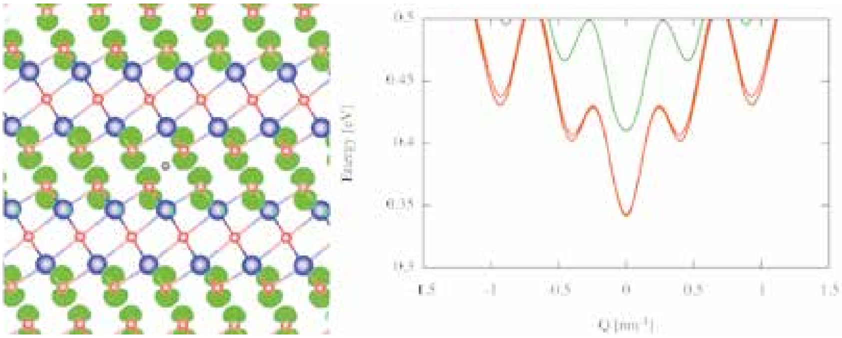


Figure 1: (Left) Wave function and (right) energy bands of topological excitons in Bi_2Se_3.

[1] M. Z. Hasan, C. L. Kane, *Rev. Mod. Phys.* **82**, 3045 (2010)

[2] Xiao-Liang Qi, Shou-Cheng Zhang, *Rev. Mod. Phys.* **83**, 1057 (2011)

[3] Flórez, F. G.; Siebbeles, L. D. A.; Stoof, H. T. C., preprint arXiv:2102.06781 (2021)

[4] D. Sangalli, *et al.*, *J. Phys. Cond. Mat.* **31**, 325902 (2020)

Artificial electronic lattices: building structures atom-by-atom

Rian Ligthart, r.a.m.ligthart@uu.nl
Supervisors: Dr. Ingmar Swart, prof. dr. Daniël Vanmaekelbergh

Sponsors : ERC Consolidator Grant
Started in: 01/10/2020

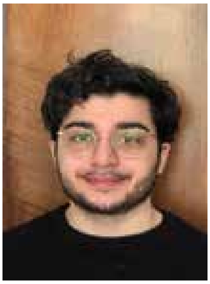
Scanning Tunneling Microscopy (STM), Artificial electronic lattices, Quantum simulator

Scanning Tunneling Microscopy (STM) can be used for imaging with atomic resolution, probing electronic properties and moving atoms with nano-scale precision. The STM is, therefore, a suitable technique for building artificial electronic lattices that function as a quantum simulator. The artificial electronic lattices consist of artificial atoms which are situated on a metallic or semiconductor crystal, e.g. Cu(111). Due to the breaking of periodicity at the surface of a metallic crystal, a surface state arises. For some crystals, the surface state can be approximated as a 2D electron gas (2DEG) which can be patterned by atomic or molecular scatterers on the surface. When the scatterers confine the 2DEG, artificial atoms can be created. The electronic characteristics of the artificial atoms can be measured in the STM and show s-like and p-like wavefunctions.

The versatile artificial atoms are used to construct lattices to study the effect of structure on electronic characteristics, thereby functioning as quantum simulator. Recently, CO molecules on Cu(111) were used to build (i) molecular graphene[1] creating massless fermions in a Dirac cone, (ii) the Sierpiński triangle[2] where the electrons behaved like they were in a fractal dimension of 1.58 and (iii) a topological insulators such as the Kekulé lattice[3] were a robust edge mode was realized. However, the CO/Cu(111) system has a lacking energy resolution due to coupling of the surface state with the bulk states. Therefore, new surfaces with scatterers are sought that can improve the electronic quantum simulator. One option that is explored are In adatoms on an InAs(111)A surface, where the In atoms create an attractive potential for the local surface state. Briefly, in this project new systems that function as quantum simulator are studied and when suitable used to probe novel effects in the quantum world!

[1] Gomes, K.K., *Nature*, **7389**, 306-310, 2012
[2] Kempkes, S. N., Slot. M. R., *Nat. Phys.*, **2**, 127-131, 2019
[3] Freeney, S.E., van den Broeke, J.J., *Physical Review Letters*, **23**, 236404, 2020

On heterobilayers of transition metal dichalcogenides



Riccardo Reho, r.reho@uu.nl
Sponsor: Sector Plan 2019 - 2024, since November 2020
Supervisors: dr. Zeila Zanolli, Prof. dr. ir. Henk Stoof
Collaborator: dr. Pedro Miguel M. C. de Melo
Theoretical spectroscopy, Excitons, 2D Heterostructures

I study optical properties of 2D multilayer structures formed by Transition Metal Dichalcogenides (TMDs). The family of semiconducting TMDs is an especially promising platform for fundamental studies of two-dimensional (2D) systems, with potential applications in optoelectronics and valleytronics due to their direct band gap in the monolayer limit and highly efficient light-matter coupling. Device prototypes with diverse functionality including phototransistors, logic circuits, light-emitting and harvesting devices have already been demonstrated. My research activity is focused on the study of vdW heterostructures build stacking multiple layers of TMDs.[1]

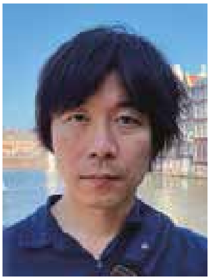
My work is to understand and be able to tell experimentalists why spectra are what they are, and what is their relation to the geometry and chemical composition of a material. I want to be able to judge whether new results are reasonable and understand the limits of validity of the theory.
I make use of first principles calculation methods to reach this goal.

I started the project studying the optical properties of two heterobilayers (HBLs) (WS_2/MoS_2 and $WSe_2/MoSe_2$) by solving the Bethe-Salpeter equation on top of a G0W0 calculation using the YAMBO code[2], which corrects the independent-particle eigenvalues obtained from ground state density-functional theory.

The reduced dimensionality of 2D structures enhance the Coulomb interaction between charge carriers leading to strongly bound electron-hole (exciton) pairs. This is interesting because the excitonic features are prominent in the optical spectra. In HBLs we can observe an exciton where the electron and the hole are situated in two different layers and we call it interlayer exciton. This lead to a natural charge separation in vdW heterostructures which can be used for the development of new photovoltaic devices.[3] The silicon era has reached its efficiency limit and these materials constitute a valid alternative. These factors motivate my research. I want to provide guidelines that tell in which way the electron–hole interaction is expected to change the spectra, and develop the analysis tools for efficient and quantitative predictions.

[1] Geim, A. K. & Grigorieva, I. V. Van der Waals heterostructures. *Nature* **499**, 419–425 (2013)
[2] D. Sangalli et al 2019 J. *Phys.: Condens. Matter* **31** 325902 (2019)
[3] E. Torun, H. P. C. Miranda, A. Molina-Sánchez, L. Wirtz, *Phys. Rev.* B **97**, 245427 (2018)

Red phosphor for high excitation flux



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Sponsor: Nichia(Japan), since January 2020
Supervisors: prof. dr. Andries Meijerink

Luminescent Materials, LED Phosphors, LD Excitation

Phosphor converted (pc-)LED is most successful technology for solid state lighting. With increasing demand for high power applications, such as projectors, high-beam headlight, and spotlight, InGaN LEDs have been faced with a problem called "efficiency droop". To overcome this issue, laser diodes(LD) are used for this field.[1]

Under high flux excitations, phosphors show a luminescence saturation. Ce^{3+}-activated garnet phosphors are widely used for high power application. However, most of garnet phosphor show green to yellow emission. This means the emission doesn't include sufficient red component. In addition, red phosphors used in conventional pc-LED, such as $(Sr,Ca)AlSiN_3:Eu^{2+}$ and $(Sr,Ba)_2Si_5N_8:Eu^{2+}$, have a poorer photoluminescence linearity in response to LD excitation than Ce^{3+} activated garnet phosphors.

The aim of this research is to develop a novel red phosphor withstanding high flux excitations.

[1] P. Zheng *et al.*, *Light Photonics Rev*. **13**, 1900147(2020)

Synthesis and characterization of colloidal semiconductor nanostructures

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Sponsor: NWO-TOP, since April 2017
Supervisor: Dr. Celso de Mello Donegá

Colloidal synthesis, Semiconductor nanocrystals, Optoelectronic properties

Despite recent advances, the synthesis of colloidal InSb quantum dots (QDs) remains underdeveloped, mostly due to the lack of suitable precursors. In this work, we use Lewis acid-base interactions between Sb(III) and In(III) species formed at room temperature in situ from commercially available compounds (viz., $InCl_3$, $Sb[NMe_2]_3$ and a primary alkylamine) to obtain InSb adduct complexes. These complexes are successfully used as precursors for the synthesis of colloidal InSb QDs ranging from 2.8 to 18.2 nm in diameter by fast co-reduction at sufficiently high temperatures (≥230 °C). Our findings allow us to propose a formation mechanism for the QDs synthesized in our work, which is based on a non-classical nucleation event, followed by aggregative growth. This yields ensembles with multimodal size distributions, which can be fractionated in sub-ensembles with relatively narrow polydispersity by post-synthetic size fractionation. InSb QDs with diameters below 7.0 nm have the zinc blende crystal structure, while ensembles of larger QDs (≥10 nm) consist of a mixture of wurtzite and zinc blende QDs. The QDs exhibit photoluminescence with small Stokes shifts and short radiative lifetimes, implying that the emission is due to band-edge recombination and that the direct nature of the bandgap of bulk InSb is preserved in InSb QDs. Finally, we constructed a sizing curve correlating the peak position of the lowest energy absorption transition with the QD diameters, which shows that the band gap of colloidal InSb QDs increases with size reduction following a 1/d dependence.[1]

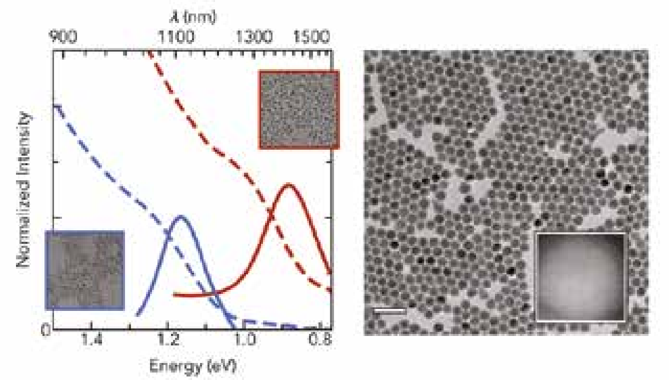

Figure 1: *Left*: Absorption (dashed lines) and photoluminescence (solid lines) spectra of colloidal suspensions of InSb QDs with average diameters of 2.9 ± 0.3 nm (blue), and 4.2 ± 0.5 nm (red). Insets: Corresponding TEM images. *Right*: TEM image of 14.9 ± 0.9 nm-InSb QDs. Inset: HRSTEM image of a 15-nm InSb nanocrystal.

[1] S. Busatto *et al.*, *ACS Nano* **14**, 13146-13160 (2020)

Experimental realization and characterization of artificial electronic lattices by scanning tunneling microscopy

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Sponsor:	ERC advanced grant, since September 2017
Supervisors:	prof. dr. Daniël Vanmaekelbergh, dr. Ingmar Swart

Scanning Tunneling Microscopy, Artificial lattices, Atom manipulation

Graphene is well known due to its many fascinating properties. The property we are most interested in is the electronic band structure, which shows Dirac cones and flat bands. These Dirac cones arise purely due to the honeycomb lattice, which means that the lattice can be made artificially from other materials than carbon atoms.

In 2012, Gomes et al. used lateral manipulation of CO molecules on a Cu(111) crystal surface to pattern a two-dimensional electron gas into a honeycomb lattice, forming artificial graphene and showing the Dirac cone.[1] We expanded on this by creating a larger, more well-defined honeycomb lattice to visualize s- and p-orbitals separated in energy. In this way, the p-orbital flat band can also be visualized and accessed. The various electronic states, amongst which the dispersionless band, could also be resolved spatially by differential conductance mapping of the wavefunctions.

Scanning tunneling microscopy (STM) is the key instrument in creating and measuring these artificial lattices. Using lateral manipulation of molecules and atoms by the STM tip we can pattern the two-dimensional electron gas on a crystal surface into nearly any shape or lattice desired. Immediately afterwards, we can perform scanning tunneling spectroscopy on this lattice and probe the electronic band structure. This technique has shown to be highly adaptable and will enable us to investigate many types of two-dimensional lattices.

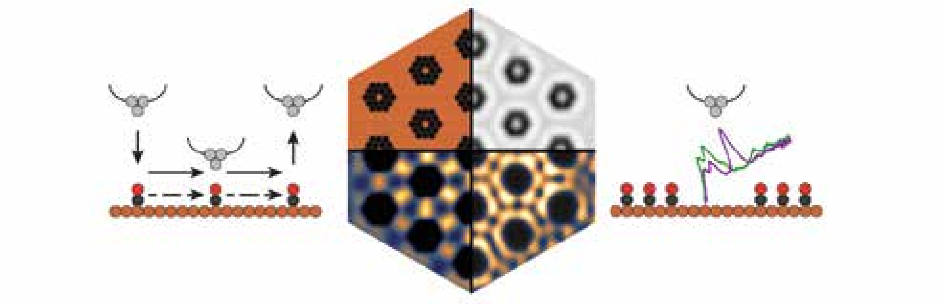

Figure 1: A schematic depiction of atom manipulation, spectroscopy and various measurements on an artificial honeycomb lattice.

[1] K. Gomes *et al.*, *Nature* **483**, 306-310 (2012)

[2] T.S. Gardenier *et al. ACS Nano* **14**, 13638-13644 (2020)

Nanoprobes for high resolution spatial and temporal temperature mapping

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Sponsor: MCEC, since December 2018
Supervisors: prof. dr. Andries Meijerink, prof. dr. ir Bert M. Weckhuysen

Nanothermometry, Lanthanide luminescence, Confocal fluorescence microscopy

Temperature determines the chemical and physical properties in a wide range of systems. Especially, in the field of catalysis this is the case, since the rate of a reaction highly depends on the temperature. Therefore, an accurate thermometer is of key importance in catalysis research. However, on the (sub-)micrometer scale the size of the thermometer often is a limiting factor for its accuracy. This can have a mechanical origin: the thermometer is larger than the probed volume or it changes the flow in a reactor. A promising method to overcome this problem is using temperature-sensing nanoparticles (NPs), which are doped with lanthanide ions (e.g. Er^{3+}, Eu^{3+}).

Luminescence from thermally coupled states in these ions follows Boltzmann behaviour. Consequently, illumination of these lanthanides followed by spectral or lifetime analysis enables accurate determination of the temperature. Using chemically inert NPs as host matrix (e.g. (SiO_2-coated) $NaYF_4$), the resolution of this technique is extended to the (sub-)micrometer scale. This is prominent method in the field of nanothermometry. A well-known composition of such nanothermometers is $NaYF_4$:Er^{3+},Yb^{3+} (Figure 1). Here, Yb^{3+} acts as an absorber of 980 nm light, whose energy is efficiently transferred to Er^{3+}. Then, the bright green luminescence of Er^{3+} is used to determine the temperature in a wide range (300–900 K).

In our work, we combine nanothermometry with confocal fluorescence microscopy to visualize the temperature in situ in relevant chemical systems like single catalyst particles and microelectronic devices.[1] Using 3D temperature maps, new insights on the activity of a catalyst can be obtained and the effect of gas flows in microfluidics can be studied. This is an unique way to investigate surface temperature at the nanoscale during catalysis. Finally, we develop new nanothermometers that operate in different ranges to extend the applicability of this technique.

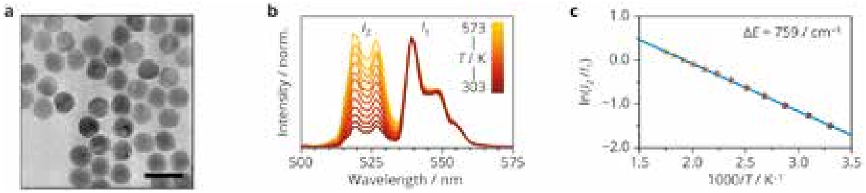

Figure 1: a) TEM image of $NaYF_4$:Er^{3+}(2%),Yb^{3+}(18%) nanoparticles. The scale bar represents 50 nm. b) Green luminescence of the nanoparticles upon 980 nm excitation. c) The logarithm of the ratio between the integrated intensities from (b) versus the reciprocal temperature (colored dots). The blue line is a fit of the experimental ratios to the Boltzmann model.

[1] van Swieten, T.P., *et al. ACS Applied Nano Mater.* **4**, 4208–4215 (2021).

Interfacial topological superconductivity

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Sponsor: Sector Plan 2019 - 2024, since January 2021
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Collaborators: R. Reho, P. M. M. C. de Melo

Spin-orbit interaction, Density functional theory, Superconductivity

Topological superconductivity, is profoundly distinct from other kinds of superconductivity.[1] Hybrid devices, composed of a conventional superconductor and a semiconductor with strong spin-orbit interaction might host topological superconductivity. For instance, one of the most exciting manifestations of topological superconductivity is the claimed possibility of hosting Majorana zero modes (MZM) at the two ends of proximitized one-dimensional nanowires. In addition to a fundamental interest in understanding Majorana physics, this field has attracted the scientific community's attention for the potential applications that these states have in fault-tolerant quantum computing. However, experimental evidence of MZM is currently debated [2-3] and topological superconductivity dramatically depends on the details of the interface [1], which are unknown or not included in theoretical models.

Density Functional Theory (DFT) calculates the electronic and structural properties of the material from first principles, without the need for empirical fitting parameters and hence, supplies significantly precise results compared to empirical methods. In this project, by utilizing DFT implemented in Quantum Espresso and SIESTA packages, we study the PbTe/Pb interface shown in Fig.1. In addition to the electronic properties, we investigated the structural parameters of each individual part of the interface and the obtained lattice constants are in good agreement with experimental values. The lattice mismatch between PbTe and Pb resulted in a strain of about 8.8% which we shared between two parties equally. By means of Kohn–Sham–Bogoliubov–de Gennes equations implemented in Siesta [4], we are investigating the proximity induced superconductivity at the interface of PbTe/Pb.

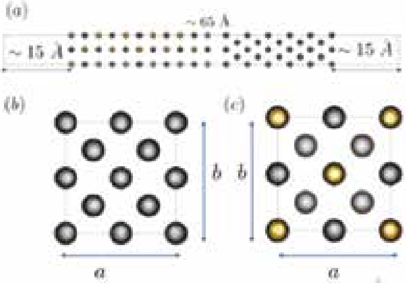

Figure 1: Ball-and-stick model of the PbTe/Pb interface along the z-direction (a) and (b-c) show the side, top and bottom view of the Pb and PbTe lattices, respectively. The strain caused by lattice mismatch is shared equally between two sides of the interface.

[1] S. M. Frolov, *et.al*, *Nat. Phys.* **2**, pages 575–594 (2020)
[2] H. Zhang, C.-X. Liu, *et.al.*, *Nature* **591**, E30 (2021).
[3] H. H. Thorp, *Science.* **373**, 500.1 (2021).
[4] G. Csire, *et.al.*, *J. Phys. Condens. Matter* **28**, (2016).

3

INORGANIC CHEMISTRY AND CATALYSIS

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Professors emeriti	prof. dr. ir. John Geus, prof. dr. ir. Diek Koningsberger
Technical support	Fouad Soulimani, Joris Janssens, Jules van Leusden, Oscar Kerkenaar, Pascal Wijten, Tim Prins, dr. Jochem Wijten
Administrative staff	Dymph Serree, Brenda Wijnen, Joke van der Kooi, dr. Martina Radli
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Sunergy	Linda Veldhuizen
PhD students/Postdocs	44

Research Mission

We do fundamental research on heterogeneous catalysts and related nanomaterials to establish the relation between structure and function on multiple length scales, ranging from the atomic level (nm) to the level of individual catalyst particles (µm) and reactors (m). We aim to understand and improve the synthesis of solid catalysts and sorbent materials and characterize them in detail during and after synthesis. We are especially interested in the development of in-situ spectro-microscopic and tomographic multi-technique approaches to study porous materials with sub-nanometre to micrometre resolution ex-situ, but also while they work under realistic conditions (i.e., operando mode). Our research is connected to major societal and environmental developments.
We pursue the development of improved catalytic routes to arrive at a more sustainable supply of transportation fuels, base and fine chemicals and functional materials (e.g., coatings), but also study the development of sustainable routes for chemical recycling, biomass conversion, and solar fuels, as well as the study of the impact of certain chemicals, such as micro- and nanoplastics, on the environment.

Fundamental insights into the kinetic behavior of supported metallocene catalysts

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Sponsor: SABIC, since July 2020
Supervisors: prof. dr. ir. Bert Weckhuysen, prof. dr. Eelco Vogt
Metallocene catalysts, Heterogeneous catalysis, In-situ spectroscopy

In our quest for polymers with superior and specialized properties, and better recyclability, better olefin polymerization catalysts are sought.

Metallocene catalysts hold great promises that are yet to be fulfilled. These zirconium (or hafnium) based catalysts are highly active, and are highly tunable through employing different ligands around the metal, and the use of co-catalysts (Fig. 1). The resulting activity in olefin polymerization can be orders of magnitude higher than catalysts of other types when used as homo-geneous catalysts.

A major challenge in utilizing these catalysts is the discrepancy (and/or deterioration) in their performance when they are transformed from homogeneous to heterogeneous catalysts. Heterogeneous catalysts are preferred by industry following decades of optimizing processes and plants around catalysts like Ziegler-Natta and Phillips catalysts to produce polyolefins. Additionally, the "single-site" character of these catalysts results in polymers that are more difficult to process into final products.

Advanced spectroscopic techniques are utilized in this project to examine the kinetic effects resulting from supporting candidate industrial metallocene catalysts. These insights are coupled with performance and activity studies in industrial settings. The aim is to explain the difference in behavior between supported (heterogeneous) and unsupported (homogeneous) metallocene catalysts.

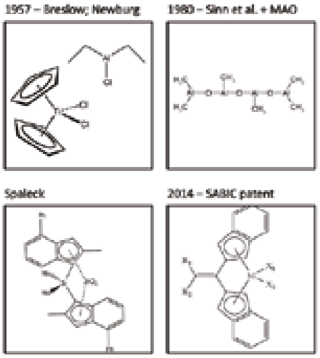

Figure 1: The evolution of metallocene catalysts for polyolefin polymerization, shown through examples.

[1] Breslow, D. S. *et al.*, *JACS* 79 **(18)**, 5072-5073 (1957)

[2] Sinn, H., *et al.*, *Angew. Chem. - Int. Ed.* **19**, 390-392 (1980)

[3] Severn, J. R. *et al.*, *Chem. Rev.* **105**, 4073-4147 (2005)

[4] Al-Shammari, H. *et al.*, patent WO2014139949A1, (2014)

Thermocatalytic conversion of industrial CO_2 waste streams into valuable base chemicals

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Sponsor: Tata Steel, M2i, NWO since October 2020
Supervisors: prof. dr. ir. Bert M. Weckhuysen, dr. Ward van der Stam
CO/CO_2 Hydrogenation, Operando vibrational spectroscopy

The metallurgical industry is still one of the largest CO_2 emitting industries, contributing to the adverse effects on the climate by elevated atmospheric CO_2 concentrations. Alternative ironmaking technologies, such as the recently developed HIsarna smelting reduction process by Tata Steel can already lower the CO2 emissions greatly, but further reduction is required.[1] The works arising gases (WAGs) of HIsarna consists of a CO_2-rich stream (~70%) at high temperature (~1500 °C), which could be ideal for direct utilization via thermocatalytic conversion reactions.

Within this project, thermocatalytic CO_2/CO hydrogenation reactions to valuable chemicals (e.g. methane, methanol, or longer carbon chains) will be explored to valorize the CO_2-rich WAGs and the heat of the HIsarna processes. The CO_2 can react with sustainable H_2 (e.g. from water splitting with excess solar or wind energy) into methane.[2] Methane can be directly used or further valorized by converting it in a second step to high-value carbon products, such as aromatics (project by Joyce Kromwijk). Ni is often considered for the methanation reaction due to its cost-effectiveness and its relative high activity and selectivity. Yet, also other metals, promotors and bimetallic systems will be tested in this project[2]. The choice of support also plays an important role in the stability and the performance of the catalyst.[3] Reducible supports, i.e. Nb_2O_5 or TiO_2, can be used to accommodate the CO present in HIsarna WAGs by stabilizing Ni with metal-support interactions and prevent the formation of toxic $Ni(CO)_4$.[4] Operando spectroscopic techniques, such as FT-IR or Raman spectroscopy will be used to monitor reaction intermediates, in order to obtain insight in the different reaction pathways. With this, we will gain fundamental understanding of the CO_2 hydrogenation reaction and contribute to the rational design of suitable CO_2 valorization catalysts from industrial point sources.

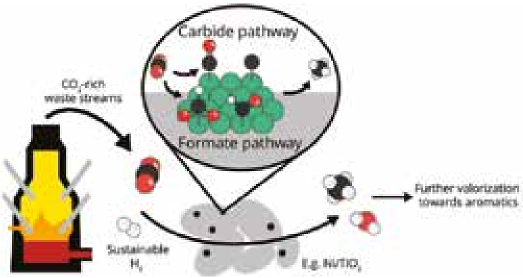

Figure 1: Schematic overview of the valorization of the CO_2-rich waste streams from the HIsarna steel making process towards methane, or further to aromatics. Vibrational spectroscopy can be used to elucidate reaction intermediates.

[1] Keys, A. *et al.*, *PBL Netherlands Environmental Assessment Agency* (2019)
[2] Vogt, C. *et al.*, *Nat. Catal.* **2**, 188–197 (2019)
[3] Vogt, C. *et al.*, *Nat. Commun.* **10**, 1–10 (2019)
[4] Hernández Mejía, C. *et al.*, *Catal. Today* **343**, 56–62 (2020)

Re-use of the byproduct hydrogen chloride to produce chloromethane over lanthanide-based catalyst materials

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HCl, operando spectroscopy, Recycling

The European market between supply and demand for HCl is in balance. However, new manufacturing plants will be built in Europe that will generate a surplus of HCl as byproduct. Therefore, alternative and sustainable routes need to be explored to find an economically feasible alternative to the unsustainable neutralization of HCl into salts and subsequently purging it into the sea.

Methane can be catalytically activated with HCl, producing valuable chlorine-containing compounds, which can be further processed to e.g. cooling agents, fuels and plastics. Very little research has been done on this topic and, as a consequence, the process has never been industrialized. The realization of such a process – by developing a more active and stable catalyst material – would close the raw material loop, reduce the carbon footprint and support the circular economy approach.

In this work, we have performed a comprehensive study on the CH_4 oxychlorination over a series of lanthanide-based catalysts with the general formula LnOCl, where Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy or Ho.[1] Central in this research project is the studying of these catalyst materials under real-life reaction conditions (Fig 1.). Advanced operando spectroscopy techniques will provide new insights in the reaction mechanism as well as valuable information enabling the design of new or improved catalysts. Furthermore, we hope to derive useful structure-activity relationships to be able to tune the product selectivity.

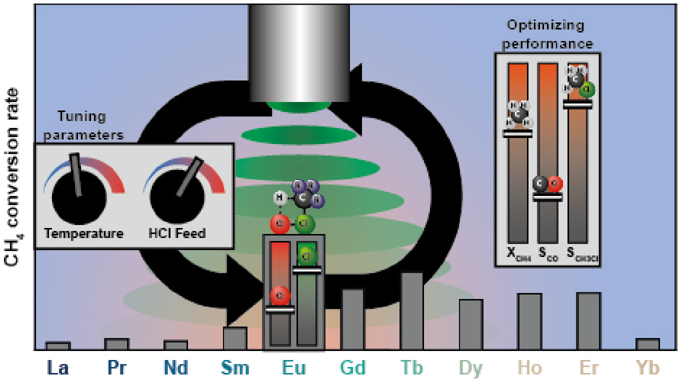

Figure 1: Table of content figure of the performed work. Various catalyst materials were tested in the Methane oxychlorination (MOC) reaction and their behavior in the reaction was studied with operando spectroscopy. By doing so, the reaction parameters could be tuned to optimize the catalytic performance of the catalyst materials.

[1] B. Terlingen *et al.*, *ACS Catal.* **11**, 10574-10588 (2021)

Operando studies of photoactive metal-organic-frameworks

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Sponsor: Austrian Science Fund (FWF), since August 2021
Supervisors: prof. dr. ir. Bert Weckhuysen

Infrared spectroscopy, Photosynthesis, Metal-organic frameworks

The rich chemistry of metal-organic frameworks (MOFs) allows to tune their light absorption to the visible region with the strongest output of the sun's irradiation spectrum. So far, photosensitizers-based MOFs rely on high power light sources and sacrificial agents. Furthermore, in depth elucidation of the reaction mechanisms that could improve the catalyst's design, is still pending.
This project will bring together precise material chemistry and inventive operando techniques to demonstrate the use of porphyrin-based MOFs for the photoconversion of solely CO_2 and water to value-added chemicals, such as methanol, formic acid or methane. The layer-by-layer synthesis of MOF films containing photosensitive organic linkers will be optimized allowing for mechanistic studies using surface-sensitive IR spectroscopic techniques in attenuated total reflection (ATR) configuration or nano-IR microscopy. These techniques will shine light on the specific adsorption sites of CO_2 reaction products and intermediates within the MOF that take place during the reaction (=operando). The photocatalyst will be further extended by organic linkers that allow for storing the photon energy chemically by generating new chemical bonds within the organic linker. Upon external triggers, the photoenergy can be released, paving the way for "photocatalysis in the dark".

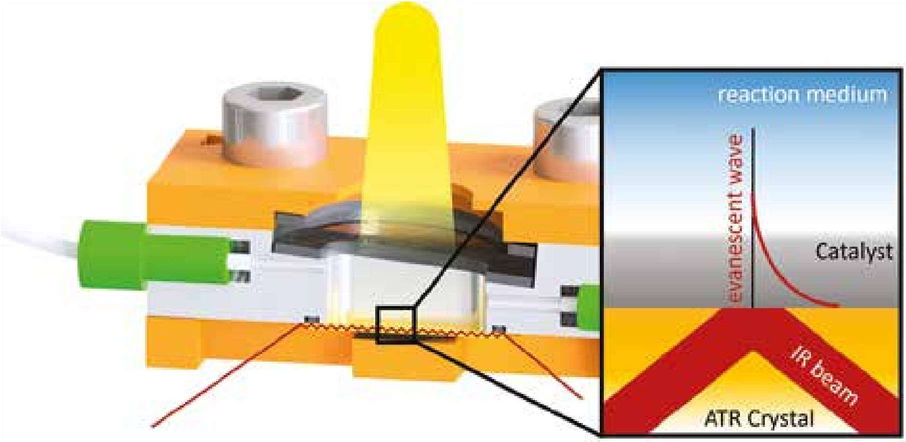

Figure 1: ATR crystal in flow cell for photocatalytic reaction monitoring. Inset: Total reflection of the IR beam at the sample/ATR crystal interface at which the evanescent wave originates that interacts with the catalyst.

Structure sensitivity and promotor effects in (de)hydrogenation reactions catalyzed by supported nickel nanoparticles

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Sponsor: BASF, since February 2021
Supervisors: prof. dr. ir. Bert Weckhuysen, dr. Ward van der Stam,
dr. Matteo Monai

Nickel, Colloidal, Catalysis

As a part of ARC CBBC, and in collaboration with BASF structure sensitivity will be investigated in nickel catalyzed (de)hydrogenation reactions, such as CO_2 methanation. Most catalytic reactions are structure sensitive, which means that the surface atoms of a supported metal catalyst differ in activity. The specific activity of surface atoms depends on their electronic structure and the atomic arrangement in their surrounding (coordination). The electronic structure and atomic arrangement are in turn influenced by the shape and size of the nanoparticle and can be tuned by the addition of promoters or modifiers. To study structure sensitivity, nanoparticles with well-defined shapes and sizes are thus necessary. In this project, nickel nanoparticles of several sizes and shapes will be synthesized to selectively expose different surfaces. Additionally, the effect of addition of other metals or functional ligands will be studied as promoters to fine-tune the properties of the nanoparticles. The synthesized nanoparticles will then be supported on high surface area supports and the catalysts will be tested in, for example, CO_2 hydrogenation, as a model structure sensitive reaction. The effect of nanoparticle shape and promoters will be studied by operando techniques such as infrared and X-ray absorption spectroscopy. This study is expected to give new fundamental insights in structure sensitivity which will guide rational design to improve catalysts for(de)hydrogenation reactions.

Visualizing the pore-network and acid sites of a fluid catalytic cracking catalyst particle

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Supervisors: prof. dr. ir. Bert Weckhuysen, prof. dr. Eelco Vogt

Heterogeneous catalysis, Fluid catalytic cracking, Confocal fluorescence microscopy

Although the Fluid Catalytic Cracking (FCC) process is being practiced for over 80 years to convert crude oil fractions into usable products, there is still a lot to learn about the mechanism behind the catalytic cracking to tune the selectivity and use more complex feedstocks. It is generally accepted that catalytic cracking involves the formation of carbenium ions and that several acid catalyzed reaction pathways can occur (parallel) which lead to the formation of the products.[1] However, the exact location of these catalytic active acid sites and the influence of the composition of the FCC catalyst particle on these acid sites for example is still studied. Imagine you are a crude oil molecule: which way will you follow through the particle and which interactions and reactions will you encounter and where?

In order to gain more insight in this we want to study the pore network, localize the acid sites and study the acidity and local environment near these acid sites in a set of FCC catalyst samples. By using Confocal Fluorescence Microscopy (CFM), a non-destructive technique capable of 3D reconstruction, we can study the properties of these particles. By performing acid-catalyzed reactions with fluorescent reactants and/or products we can localize the acid sites and by using (chemosensitive) fluorescent probes we can study the local environment and pore network in these FCC catalyst particles.[2],[3],[4]

However, due to the dense structure of the FCC catalyst particles, the resolution in the z-direction is limited because of self-absorption and scattering of the light. To study the interior of the particles more in depth we want to use (cryo-)microtoming to cut the particles open and make thin slices to also correlate the morphology to fluorescence data with electron microscopy. Another approach would be to make thin FCC films by spincoating.[5] In this way all components of a FCC catalyst particle are present and hopefully mimic the situation of an industrial spherical FCC catalyst particle so we can more easily study the acid sites and local environment using CFM without cutting the particle.

[1] E.T.C. Vogt, *et al.*, *Chem. Soc. Rev.* **44**, 7342-7370 (2015)
[2] M.M. Kerssens *et al.*, *Microporous Mesoporous Mater.* **189**, 136-143 (2014)
[3] F.C. Hendriks *et al.*, *Chem. Eur. J.* **23**, 6305-6314 (2017)
[4] I.L.C. Buurmans *et al.*, *Chem. Eur. J.* **18**, 1094-1101 (2012)
[5] Lam *et al.*, *Cracking Catalyst Composition*, United States Patent US 2002/0165083A1, United States Patent Application Publication, Nov. 7, 2002

Metal organic framework based catalysts for sensing and destruction of volatile organic compounds (VOCs)

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Sponsor: MCEC, since April 2019
Supervisors: prof. dr. ir. Bert M. Weckhuysen, dr. Florian Meirer

MOFs, UiO-67, Heterogeneous catalysis, VOCs

Metal-Organic Frameworks (MOFs) are organic-inorganic hybrid crystalline porous materials that consist of organic bridging ligands or linkers, coordinated to metal-base nodes to form an extended network with uniform pore diameters typically in the range of 3 to 20 Å.[1] The choice of metal and linker dictates the structure and the properties of the MOF. UiO-67 is a zirconium based MOF bridged to biphenyl-4,4′-dicarboxylic acid linker, where the later can be modified to create defects within the structure.

The aim of this project is to be able to create thin-film UiO-67 MOFs with functionalities and study their catalytic activity as films on surfaces compared to solid crystals in reactors. Understanding the active sites and their dynamics is extremely important in order to design and develop better ones. This is done by using a recently acquired Photoinduced Force Microscopy (PiFM) as well as other chemical imaging methods to investigate thin-film MOF materials in great detail. The core focus of this project will be focused towards the synthesis and characterization of newly developed SURMOFs (Surface-Bound MOF materials). This will be done by trying different synthesis approaches and comparing results obtained by several spectroscopic and analytical techniques, on different types of substrates. Moreover, the work will be extended to catalytic studies, mainly focusing on photocatalysis and catalytic reactions in the gas-phase, including but not limited to air pollution control.

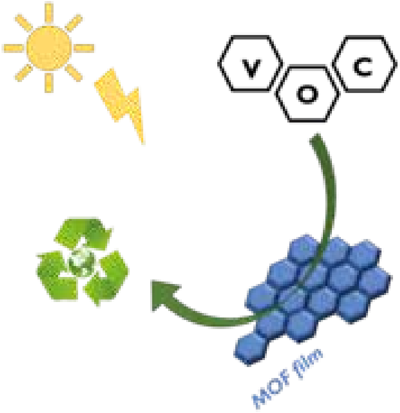

Figure 1: Photocatalysis reaction scheme on MOF film.

[1] Kalidindi, S. B. *et al.*, *Angew. Chem. Int Ed.*, **54**, 221–226 (2015)

Luminescence thermometry for operando monitoring of local temperatures during endothermic and exothermic hydrocarbon conversion processes

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Supervisors: Prof. dr. ir. Bert Weckhuysen, Dr. Freddy Rabouw
Oxidative coupling of methane, Luminescence thermometry, Operando spectroscopy

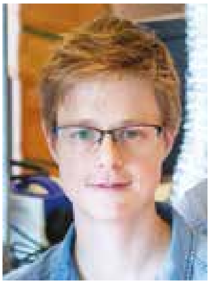
The main focus of my research is to develop high temperature luminescence thermometry techniques and apply them within the field of heterogeneous catalysis. For strongly exothermic or endothermic reactions, the local catalyst surface temperature can vary significantly from the average reactor temperature. In addition, strong temperature gradients can exist over the catalyst bed. On the one hand, exothermic reactions can result in hot spot on the catalyst, leading to poor product selectivity or even reactor runaways. On the other hand, endothermic reactions can result in a lower effective temperature at the catalyst surface, leading to underperformance of the catalyst. Luminescence thermometry is a promising technique to non-invasively monitor local temperatures with high precision.[1]

A typical reaction that is interesting to study with luminescence thermometry, is the oxidative coupling of methane (OCM). In this reaction, methane is converted into ethane and, more importantly, ethylene. Despite inherent challenges in this reaction, related to C-H bond activation in both reactant and products, high temperature requirements, and a delicate balance between activity and selectivity, direct conversion of methane into vital chemicals such as ethylene remains a process that holds great promise.[2] In addition to this catalytically interesting prospect, OCM is a perfect model reaction for the further development of luminescence thermometry techniques, due to the high exothermicity of reaction and high reaction temperatures of up 1000°C. This combination makes the OCM process an ideal stepping stone to redefine the boundaries of luminescence thermometry for operando reaction monitoring while at the same time facilitating detailed research of direct methane conversion.

In order to apply luminescence thermometry in the OCM process, microcrystalline rare earth oxides are chosen as model catalysts and europium is chosen as temperature sensor. Rare earth oxides are known to show activity towards oxidative methane coupling, as well as being a good host material for luminescent Eu_{3+} ions. Upon excitation with ultraviolet light, these ions show temperature dependent luminescence in the visible part of the electromagnetic spectrum over a wide temperature range. With fiber-coupled spectroscopy instruments, we are able to measure the temperature-dependent europium emission from inside an operational reactor, while analyzing the products of reaction via on-line gas chromatography.

[1] D. Jacques, *et al.*, *Nanoscale* **4**, 4301-4326 (2012)
[2] Y. Gambo *et al.*, *J. Ind. Eng. Chem.* **59**, 218-229 (2018)

Support, alloying and promoter effects on active sites in CO_2 hydrogenation over nickel catalysts



Ellen Sterk, e.b.sterk@uu.nl
Sponsor: MCEC, since February 2019
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CO_2 Hydrogenation, Nickel catalysts, Theoretical chemistry

Due to an increase of the CO_2 level in our atmosphere and its associated negative impact on our climate, CO_2 activation and valorization has gained a lot of attention recently. The use of CO_2 as C-containing feedstock can be a means for the abatement of CO_2 as an environmental pollutant during the search for fossil fuel alternatives.

CO_2 methanation over supported nickel nanoparticles, also known as the Sabatier reaction, is a catalytic reaction with the potential to reduce the negative environmental impact of CO_2 point sources and at the same time increase the large-scale applicability of renewable electricity. Previous work has shown that this reaction is structure-sensitive.[1] This means that both the reaction mechanism and the catalytic activity of Ni surface atoms depend on their local environment.[2] To visualize the concept of local environment, the structural identification of nickel surface atoms of four nickel facets is depicted in Figure 1.

Particularly crucial to a better understanding of the structure-sensitivity of the Sabatier reaction over nickel catalysts is to understand all relevant elementary reaction steps over the various exposed nickel metal facets, because this will tell which type of facets and which elementary reaction steps are curial for an efficient nickel methanation catalyst. These insights can be used as a starting point for rational catalyst design in order to further optimize the activity of nickel catalyst in CO_2 hydrogenation and to investigate the effects of alloying and promoter materials in order to change product selectivity.

In my PhD research I will use *ab-initio* simulation methods to uncover the fundamental aspects of this structure-sensitive catalytic reaction. This project is a collaboration between University of Utrecht and Eindhoven University of Technology within the MCEC consortium.

Figure 1: Schematic representation of CO2 methanation over four nickel facets. Surface atoms with a same structural identification are represented with matching colors.

[1] C. Vogt *et al.*, *Nat. Commun.* **10**, 5330 (2019)
[2] R.A. van Santen, *Accounts of Chemical Research* **42**, 57-66 (2009)

Pore space characterization of a single catalyst particle using fluorescent reporters

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Fluorescence microscopy, Pore space characterization, Mass transport

Porous solids are widely used in adsorption, molecular separation, and catalytic conversion processes. The performance of these materials frequently depends on the diffusivity of guest molecules through their pores; therefore, understanding of the underlying processes and pore space is not only of fundamental, but also of industrial and societal importance.[1] In this research project, we use fluorescent probes to trace mass transport through porous solids and to characterize the solids' pore space. We follow the motion of single probes or their ensemble movement to study the interaction between the pore space and the fluorescent reporter. Either this reveals directly how mass transport is affected by the local pore space, or indirectly by characterization of the pore space via pore–probe interactions. For example, using super-resolution single-molecule tracking, we have shown how the molecular movement of fluorescent oligomers is affected by the pore geometry of industrially important ZSM-5 zeolites.[2] To gain fundamental insight into pore–probe interactions, we track the motion of quantum dot probes in well-defined artificial pores constructed with nanolithography. Ultimately, our goal is to use the trends found in this controlled environment to characterize complex solids with an unknown pore space. In another approach, we use the fluorescence emission of the reporters as a sensor for the local pore environment. For instance, we have investigated a molecular reporter that changes its fluorescence behaviour when confined in the zeolite's micropores, which we have exploited to map real-time diffusion into a single zeolite crystal. Spectral changes in the photoluminescence also allow us to specifically map the surface properties of the pores, such as acidity and hydrophilicity. For practical applications, zeolite crystals are usually embedded in a matrix of oxidic compounds, such as silica, alumina and clay, forming a complex hierarchical catalyst particle. Herein, zeolite aggregate domains with seemingly identical structural features have been shown to exhibit significantly different reactivity .[3] Building on this research work, we correlate the fluorescence emission of fluorescent carbon dot reporters with scanning electron microscopy micrographs to link the surface properties to the morphology of the zeolite and their surrounding matrix. By looking both bottom-up and top-down, we are building a complete picture of the pore space of a single catalyst particle.

[1] J.J.E. Maris *et al.*, *Adsorption* **27**, 423–452 (2021)
[2] D. Fu, J.J.E. Maris *et al.*, *in preparation* (2021)
[3] F.C. Hendriks, *et al.*, *Angew. Chem. Int. Ed.* **57**, 257–261 (2018)

Unraveling the fundamentals of metal synergy in supported bimetallic catalysts

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Sponsor: ARC CBBC, since June 2019
Supervisors: prof. dr. ir. Bert Weckhuysen, dr. Ward van der Stam,
dr. Matteo Monai

Bimetallic catalysts, Rational catalyst design, Metal synergy

The replacement of scarce noble metals by base metals in catalyst formulations is a fundamental challenge for sustainability in catalysis, which has to be tackled by a multitude of approaches. Although nickel catalysts have been applied in many processes in the past, the requirements for novel processes often cannot be met by base metals alone. For some reactions, the superior activity, selectivity, or stability of noble metal catalysts leaves no alternatives, despite their high price, as can be seen for various industrial processes.[1] However, the combination of metals and the exploitation of their synergy offers the potential to almost entirely replace them and simultaneously outperform their monometallic counterparts as can be seen for Pd-Ni catalysts in a variety of reactions ranging from biomass conversion to electrocatalysis.[2]-[6]

The fundamental understanding of these catalysts is an inevitable step to design novel catalysts for future processes like the valorization of biomass or even off-gases. By studying catalysts under operando conditions as well as their genesis we can gain insights on their dynamic structural evolution and link those insights with their performance. By linking these structure-performance relations with alterations in the synthesis procedure we will contribute to the concept of rationally designing bimetallic catalysts.

[1] Twigg, M. V. *et al., Eds.*, CRC Press, (**2018**).
[2] Zhang, J. W. *et al., Green Chem.*, 18, 6229-6235, (**2016**) .
[3] Steinhauer, B. *et al., Appl. Catal. Gen*, **366**, 333-341, (2009).
[4] Huynh, T. *et al., Electrochem. Commun.,* 101, 93-98, (**2019).**
[5] Feng, Y.-S. *et al., Chin. Chem. Lett.*, 26, 709-713, (**2015).**
[6] Zhang, L.-J. *et al., J. Chem. Res.*, 42, 419-423, (**2018).**

Near-field spectroscopic imaging of the assembly and working of surface-mounted metal-organic frameworks

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Sponsor: ERC Advanced Grant, since September 2016
Supervisors: prof. dr. ir. Bert Weckhuysen
Metal organic frameworks (MOF), Surface-mounted MOF (SURMOF), Near-field spectroscopy

The pressing need for a more sustainable society has sparked intensive efforts in search for novel materials with controlled structure, porosity and functionalities. Such porous materials may combine high catalytic activity and selectivity with a long-term stability in the conversion of both renewable (e.g. biomass) and non-renewable feedstock when producing future transportation fuels, chemicals and pharmaceutical intermediates.

In particular, metal-organic frameworks (MOFs) show potential for rational catalyst design. Due to their build-up of distinct metal ions and interchangeable organic linkers they possess a highly tuneable nature. Therefore, the goal of this research is to obtain new fundamental insights in their formation principles and catalytic functioning.

To do so, nano-sized sheets of MOF materials will be constructed as model systems amenable to nano-spectroscopic research. To this end, Au substrates will be functionalized with thiol-based self-assembled monolayers (SAMs). These are able to orient the growth of MOFs being grown by liquid phase epitaxy (LPE), or layer-by-layer growth (LbL).[1] The self-assembling behaviour of these SAMs is studied minutely to explore the possibility of non-lithographic SURMOF patterning. Furthermore, the effect of the variation of LbL synthesis parameters, such as temperature, precursor solution dilution, and growth time, will be studied.[2]

Novel analytical tools, such as scanning probe methods together with IR spectroscopy (AFM-nanoIR), or Kelvin probe force microscopy (KPFM), are used to establish structure-property relationships. These novel tools and models will be used to study the chemistry of synthesis, self-assembly and catalysis.[3] By combining these synthesis and characterization techniques, intricate catalyst surfaces can be designed while circumventing the use of expensive "top-down" approaches.

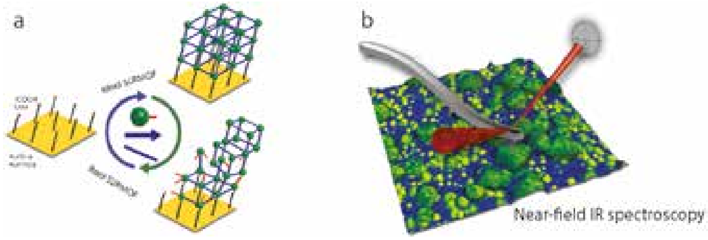

Figure 1: A) Growth of a metal-organic framework SURMOF on a functionalized Au substrate. B) Working principle near-field spectroscopic IR technique.

[1] O. Shekhah *et al.*, *Angew. Chem. Int. Ed.*, **48**, 5038-5041 (2009)
[2] G. Delen, *et al.*, *Chem. Eur. J.*, **24**, 187-195 (2017)
[3] D. Fu *et al.*, *Chem. Comm.*, **53**, 13012 – 13014 (2017)

Synthesis and characterization of dihydrogen monoxide

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Sponsor:	Utrecht University, since June 2019
Supervisor:	prof. dr. ir. Bert Weckhuysen

Electrocatalysis, Raman spectroscopy, CO_2 conversion

Copper (Cu) is a unique metal due to its outstanding ability to produce ethylene and other C_{2+} products in the electrocatalytic CO_2 reduction reaction (CO2RR). However, the exact reaction mechanism for C_{2+} products is complex and still debated in literature. Both the structure of the electrode surface and the chemistry of surface intermediates are considered to be important performance-deciding factors. However, many crucial details still remain unclear. Such processes may happen on a timescale near or below one. Therefore, *in situ* time-resolved spectroscopic techniques are necessary to gain more insight into the reaction mechanisms.

In situ Raman spectroscopy has seen many successful applications in aqueous environments. Surface Enhanced Raman Spectroscopy (SERS) can be further exploited to boost the sensitivity towards adsorbed. Interestingly, Cu is known to exhibit strong SERS activity next to its unique electrocatalytic abilities for C-C coupling and C_{2+} product formation. This allowed us to achieve sub-second in situ time-resolved SERS under CO_2RR conditions, revealing details of dynamic surface reconstruction of Cu as well as chemical processes of adsorbed CO in real-time.

Our experiments reveal that anodic treatment (1.55 V, all potentials are vs. RHE) and subsequent reduction (<-0.4 V vs. RHE) roughens the electrode surface, resulting in hot-spots for enhanced SERS activity, as well as a 4x increase in CO-coupling efficiency towards C_{2+} products (at -1.0 V vs. RHE). A dynamic CO intermediate around 2060 cm^{-1} is correlated to the production of ethylene at a cathodic bias of -0.9 V vs. RHE. At less cathodic bias (-0.7 V vs. RHE), the Raman spectra are dominated by a static vibrational signature at 2092 cm^{-1}, which is ascribed to CO on undercoordinated sites, resulting in gaseous CO production. Our results display that CO_2RR and their intermediates are dynamic, and showcase the need for improved time-resolved in situ spectroscopic investigations down to milliseconds in order to investigate the reaction kinetics in detail[1].

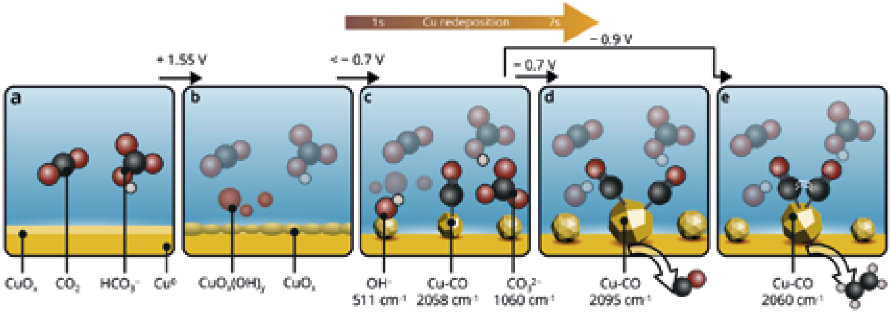

Figure 1: Evolution of a polycrystalline Cu catalyst during CO_2RR as revealed by in-situ time-resolved SERS.

[1] H. An *et al.*, *Angew. Chem. Int. Ed.* **60**, 16576-16584 (2021).

Revealing the band structure of metal halide perovskites and its implications for photocatalysis

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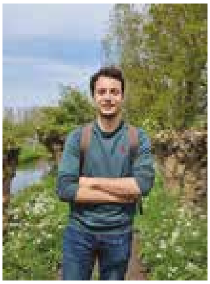
Sponsors: NWO VI.Veni.192.034., ARC-CBBC

Supervisors: dr. Eline Hutter, prof. dr. ir. Bert Weckhuysen

Perovskites, Photocatalysis, Transient absorption spectroscopy

Metal halide perovskite (MHP) semiconductors, such as methylammonium lead iodide, have recently received tremendous attention in materials science, as these have yielded high efficiency solar cells, X-ray detectors and LEDs. However, one of the most fundamental material properties of MHPs still remains debated: whether their bandgap is direct or slightly indirect. The nature of the bandgap determines both the light absorption properties and the lifetime of light-generated charge carriers. Both of these properties are important for e.g. the efficiency of a solar cell or the suitability of MHPs to be used as photocatalysts. For this research we aim to reveal the nature of the bandgap and investigate whether this can be manipulated. To do so, we will study the absorption of light and the recombination of charge carriers as a function of temperature and pressure using different optical spectroscopy techniques. Furthermore, we will make a link between the bandgap and the photocatalytic activity of MHPs. Finally, we will study lead-free perovskites, like silver-bismuth double perovskites, as these are less toxic, which is of importance considering its potential application in photocatalysis.

Towards a multifunctional catalyst for the hydrogenation of iso-oleic acid to ultrastable isostearic acid



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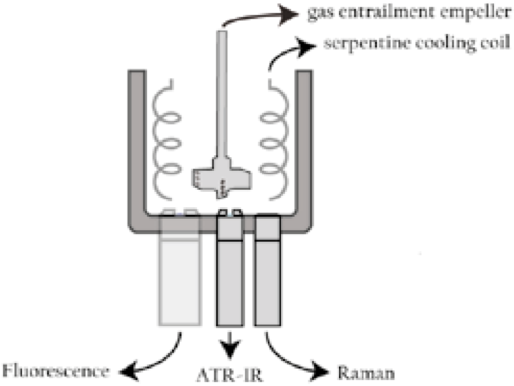
Sponsor:	Croda, BASF, VibSpec, since April 2021
Supervisors:	prof. dr. ir. Bert Weckhuysen, prof. dr. Eelco Vogt

Hydrogenation, Spectroscopy, Industrial

My project is part of the NWO-LIFT programme and is a collaboration with Croda, BASF and Vib-Spec.

Isostearic acid is a naturally-derived chemical found in various applications such as cosmetics, foods and lubricating oils. Its commercial production takes place through the hydrogenation of the fatty acid iso-oleic acid, which can be made from vegetable oils.

The aim of this project is to develop a bifunctional solid catalyst which, in addition to the hydrogenation reaction, also removes undesired colour and odour compounds from the reaction mixture. This catalyst should produce high purity isostearic acid and should furthermore remain stable for extended amounts of time. To study the hydrogenation process, a combination of in-situ characterization methods will be installed in the reactor, such as ATR-IR, Raman and fluorescence spectroscopy. These techniques will then be complemented with off-line methods, such as GC-MS and NMR spectroscopy.



Nanoplastics: origin, structure, and fate

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Supervisors: prof. dr. ir. Bert Weckhuysen, dr. Florian Meirer

Nanoplastics, Pollution, PiFM

It was recently estimated that about 99% of the plastic in the ocean remains undetected. [1] Much of this missing plastic is hypothesized to be the result of plastic degradation into micro- and nanoplastics, which is an even greater potential threat to the environment compared to the floating plastic, as it can be easily ingested by animals and humans.[2]

Microplastics have received a lot of research attention [3] and have previously been shown to be degradation products from larger pieces of plastic. However, the degradation process does not stop at the micron scale, but microplastics continue to degrade into nanoplastics,[4] which are below the detection limits of commonly available collection and identification methods. In addition, little is known about the effects of nanoplastics on the ecosystem. In order to properly tackle plastic pollution in the environment and to evaluate possible damage to humans and animals down to the microbial basis of the food web, it is crucial to set up a toolbox that enables the detection of nanoplastics. Unfortunately, moving from detecting and studying microplastics to nanoplastics is not as easy as one might think.

In this research project, we aim to detect and characterize these nanoplastics that are proposed to be a potentially important sink for the "missing" plastic fraction by developing methodologies to confirm their presence and determine their chemical and physical properties. One of the main techniques used here is Photo-induced Force Microscopy (PiFM), which combines the principles of Atomic Force Microscopy (AFM) and infrared (IR) spectroscopy (Figure 1).[5] As a result, topographic or morphological information can be obtained simultaneously with nanoscale chemical information.

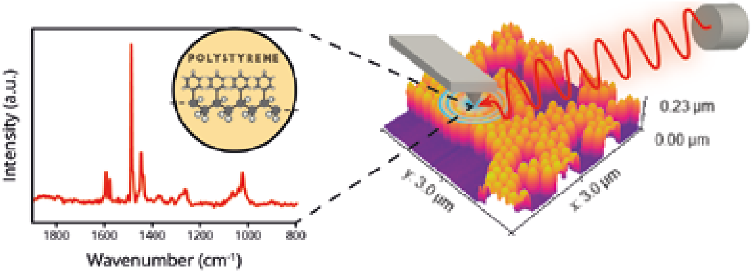

Figure 1: Schematic representation of detecting nanoplastics with PiFM.

[1] E. van Sebille *et al.*, *Environ. Res. Lett.* **10**, 124006 (2015)
[2] *Nat. Nanotechnol.* **14**, 299 (2019)
[3] K. Pabortsava *et al.*, *Nat. Commu.* **11**, 4073 (2020)
[4] A. Dawson *et al.*, *Nat. Commu.* **9**, 1001 (2018)
[5] I. ten Have *et al.*, *Chemistry—Methods* **1**, 205-209 (2021)

CO_2 Electroreduction: searching for the key to unlock the formation of C_{2+} hydrocarbons with operando vibrational spectroscopy

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CO_2 electroreduction, Surface Enhanced Raman Spectroscopy

Carbon dioxide (CO_2) could be a promising carbon source to produce chemical building blocks. As big chemical processes release significant amounts of CO2 in the atmosphere, it would be a waste not putting effort in finding novel processes to valorize CO2, as it could serve as a cheap and alternative carbon feedstock in our chemical industry.

Electrochemical reduction of CO_2 in aqueous solution using copper electrodes and (renewable) electricity to common chemicals, such as the C_1 products carbon monoxide and methane, or the C_2 products ethylene and ethanol, has already been reported with high Faradaic efficiencies.[1,2] Although we know that copper has the unique ability to induce C-C coupling, production of C_{3+} compounds with high Faradaic efficiencies has not been reported yet. The kinetic pathways, and how we can control the selectivity and stability of CO_2 reduction to higher hydrocarbon chains are knowledge gaps and ask for more extended research. In this research, we will unravel these knowledge gaps regarding the kinetic pathways of CO_2 reduction and try to enhance the product selectivity (including to higher hydrocarbons C_{3+}) and activity. This involves surface characterization using time resolved and high spatial resolution surface sensitive techniques that could lead to in situ visualization of reaction intermediates and special changes. This will be realized using in situ surface-sensitive IR and Raman spectroscopy on copper and copper oxide nanoparticle (pure and alloys) electrodes as illustrated in Figure 1.

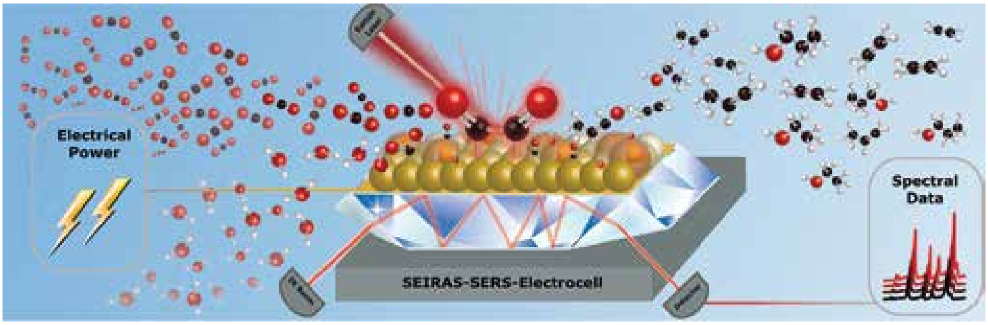
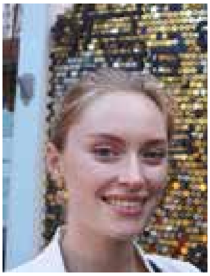


Figure 1: Illustration of operando vibrational spectroscopy on CO_2 electroreduction. CO_2 is reduced and with H2O, various C_{2+} products can be formed. The vibrational data provides detailed information on intermediate species on the surface, which helps to elucidate the reaction kinetics and pathways.

[1] S. Nitopi *et al.*, *Chem. Rev.*, **119**, 7610–7672 (2019).
[2] Y. Yuvraj Birdja *et al.*, *Nat. Energy*, **4**, 732–745 (2019).

Elucidating the role of late transition metals as promotor elements in noble metal-based redox catalysts



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Supervisors: prof. dr. ir. Bert Weckhuysen, prof. dr. Eelco Vogt

Automotive catalysis, CO oxidation, Platinum

The shift away from combustion-only car engines to hybrid cars results in much lower temperatures of the exhaust gasses, for which existing Platinum Group Metal (PGM) exhaust catalysts, such as the diesel oxidation catalyst (DOC), are not optimized. Addition of promotor materials, such as a wide range of cations, is known to change the electronic properties of catalytic Pt nanoparticles, thereby changing the CO oxidation temperature.[1] New Pt-based catalysts promoted with late transition metals have recently been developed, which are capable of lowering the CO oxidation temperature, even in the presence of other exhaust gasses such as hydrocarbons and water. The aim of this project is to gain understanding into the metal-promotor and metal-support interactions governing this reaction by developing and employing innovative in-situ and operando characterization techniques based on X-ray, vibrational and luminescence spectroscopy, allowing the Pt-based catalyst to be tested under realistic DOC reaction conditions. A combination of industry-based samples and laboratory-made samples will facilitate gaining new information on promotor-metal-support interactions. For example, new sensors will be developed based on Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy and Bandshape Luminescence Thermometry to simultaneously study the adsorbed surface species, as well as local temperature during CO oxidation reaction conditions. On top of that, the newly developed Pt-based catalysts will also be tested in the propane dehydrogenation reaction.

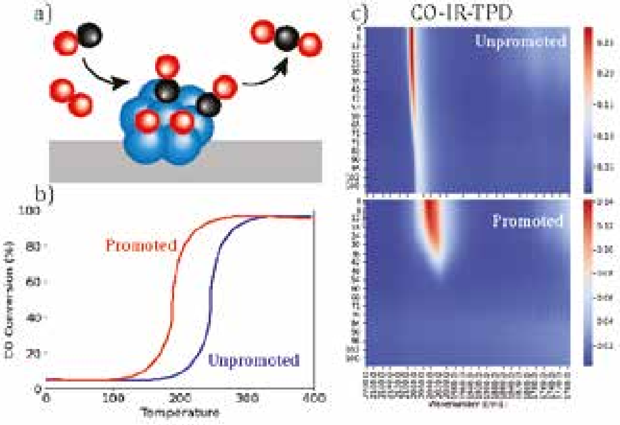
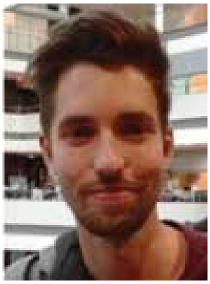


Figure 1: a) Schematic representation of CO oxidation on a Pt nanoparticle. b) Schematic representation of the effect of promotion on the light-off temperature of CO oxidation. c) Effect of promotion on CO-Temperature Programmed Desorption monitored by IR.

[1] T. Visser *et al.*, *J. Phys. Chem. B* **109**, 3822–3831 (2005)

Synthesis, characterization & fragmentation behavior of porous metallocene supports for the production of impact copolymers of polypropylene



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Sponsor:	TotalEnergies, since December 2019
Supervisors:	prof. dr. ir. Bert Weckhuysen, prof. dr. Eelco Vogt

Polymers, X-ray microscopy, Confocal fluorescence microscopy

Shell-Isolated nanoparticle-enhanced raman spectroscopy for catalysis research

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Sponsor: MCEC
Supervisors: prof. dr. ir. Bert M. Weckhuysen
Surface-enhanced raman spectroscopy, Catalysis, Model catalysts

Surface Enhanced Raman Spectroscopy (SERS) is a specialized type of Raman spectroscopy which utilizes metal nanostructures to greatly enhance the Raman signal. In 2010 Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy (SHINERS) was introduced by the group of Tian which utilizes a thin metal oxide layer to isolate the metal nanostructure from the measured substance.1 Thereby greatly improving the capabilities of SERS in catalysis research. Since this influential publication, SHINERs has proven to be a valuable tool in catalysis research for monitoring surface chemical species.

In this research SHINERs is used to study model systems consisting of catalytic nanoparticles (transition metal, 1-5nm) deposited on silica coated gold nanoparticles (~80nm). Spark ablation is a novel technique to produce these catalytic nanoparticles ligand free in gas phase, with excellent control over particle size. In this way the effect of particle size on catalytic activity can be studied.

To improve the reproducibility of SHINERs experiments new substrates were developed consisting of monolayers of shell-isolated gold nanoparticles, see Figure 1b-c. These substrates show reproducible and homogeneous Raman signal enhancement. Moreover, a catalyst can be added through impregnation with a metal precursor solution, and catalytic reactions such as CO oxidation can be studied *in situ*, see Figure 1d.

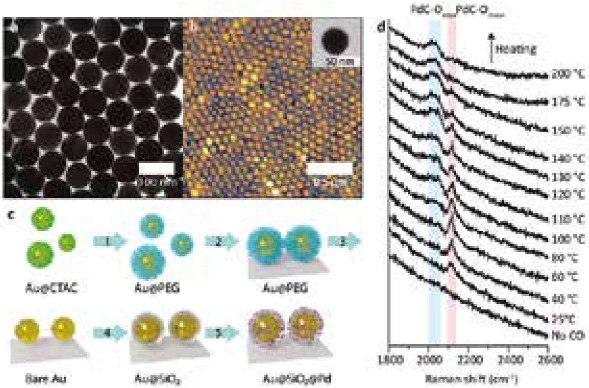

Figure 1): Homogenous SHINER substrates for applications in catalysis. (a) Transmission electron microscopy image of highly spherical gold nanoparticls. (b) Atomic force microscopy image of a monolayer of polymer (PEG) functionalized gold nanoparticles. (c) A schematic of the procedure to obtain homogenous Raman enhancing substrates. (d) *In situ* Raman measurement of CO oxidation on a Pd catalyst using the new substrate.

[1] Z. Q. Tian *et al. Nature* **464**, 392–395 (2010)

Two-step thermochemical CO_2 hydrogenation toward aromatics

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Sponsor:	Tata Steel and M2i, since January 2021
Supervisors:	prof. dr. ir. Bert Weckhuysen, dr. Ward van der Stam

Heterogeneous catalysis, CO_2 valorisation, Autothermal reactor

The metallurgical industry is one of the largest CO_2 emitting industries. In order to reduce the CO_2 footprint of the steel production process, Tata Steel developed HIsarna: a process which reduces the CO_2 emission by 20%. The Works Arising Gases (WAGs) of the HIsarna have a high CO_2 content, but also contain CO, H_2O, metal particulates and sulfur containing compounds. On top of that, the temperature of the HIsarna stream is very high (~1500°C).[1] The CO_2 footprint of the steelmaking process can be further reduced by valorizing these CO_2-rich WAGs.

The goal of this project is to investigate two solid catalysts for a two-staged thermochemical CO_2 hydrogenation reaction: CO_2 will be converted into methane and subsequently into aromatics via the methane dehydroaromatization (MDA) reaction, as shown in Figure 1. An autothermal reactor will be designed to take advantage of the high-temperature of the HIsarna WAGs to drive the strongly endothermic MDA reaction (CH_4 to aromatics).

One of the main challenges of this project is to find stable catalysts that are resistant against the poisons present in the HIsarna stream. CO_2 methanation over nickel-supported catalysts has been extensively studied due to their excellent catalytic performance and low cost.[2] On the other hand, Mo supported on ZSM-5 is the catalyst of choice for the MDA reaction.[3] However, the HIsarna waste stream contains components that act as poisons for these catalysts and can severely affect the performance. Not only metal particulates and sulfur containing compounds can poison the catalysts, but also the high amount of steam present will form an issue for the zeolite-based catalyst for the conversion of methane into aromatics. Therefore, the effect of these poisons on the catalysts will be studied with techniques such as XRD, solid state NMR and operando UV-Vis spectroscopy which will eventually lead to the valorisation of waste streams in the steel industry.

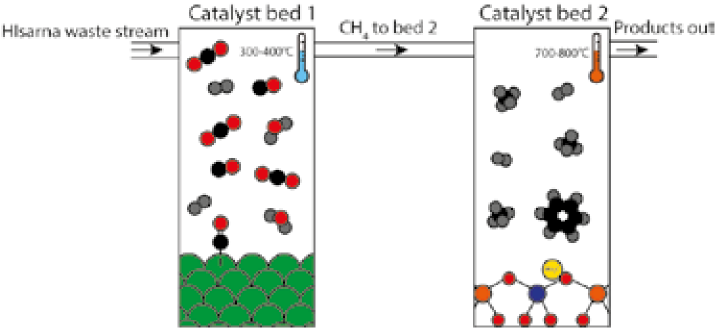

Figure 1: Two-staged thermochemical conversion of CO_2 into aromatics.

[1] A. Keys, , *et al.*, Decarbonisation options for the Dutch Steel Industry, PBL Netherlands Environmental Assessment Agency & ECN part of TNO, The Hague (2019)

[2] I. Vollmer *et al.*, *ChemCatChem* **11**, 39-52 (2019)

[3] E. Vogt *et al*, *Nature Catalysis* **2**, 188-197 (2018)

Coatings and functional materials – controlled catalytic breakdown of chitin to waterborne building blocks

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Supervisors:	prof. dr. ir. Bert Weckhuysen, dr. Ina Vollmer

Depolymerization, Crosslinking, Nanoscale spectroscopy

The application of coatings comes nowadays along with a high consumption of solvents to enable an easy treatment of the coating substance. As organic solvents are polluting the environment and pose a health risk on people working with coatings, systems which are based on water would be a highly attractive alternative and are therefore of rising interest for the research. The by now known waterborne systems still have crucial limitations like weak thermal stability and water sensitivity, which makes them appear rarely in every-day applications.

I am therefore working on the controlled breakdown of bio-based polymers with a stable backbone like chitin, which is further tuned to an ideal building block for the subsequent binder formation for a waterborne coating. Together with PhD students from other universities and industry partners, the aim is to find new concepts for the design and synthesis of durable and functional water-based coating products based on biopolymers.

Therefore, optical characterization techniques will be used to explore both the catalyst-solvent combinations for depolymerization as well as the solubility and functionalization of the resulting building blocks. Further on, the film formation and drying processes of the waterborne coatings will be examined with AFM-IR to use it as a feedback loop for fine-tuning of the experimental conditions of the depolymerization processes.

Characterization of micro- and nanoplastics for early-life health risk assessment

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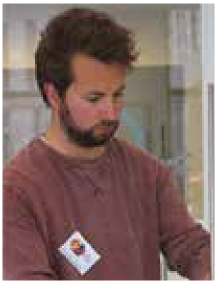
IR-spectroscopy, Atomic force microscopy, Environmental health

Each year, large amounts of plastic waste are finding their way into the environment. We have all seen that large pieces of plastic are dangerous to several kinds of animals, but these large pieces can also break down into so-called microplastics, or even smaller, nanoplastics. Little is known about their chemistry, morphology and their possible health effects for mankind. Especially for embryos, these health effects should be mapped out, since they are such small organisms and fetal development is such a complicated process.

My project focuses on the in-depth characterization of micro- and nanoplastics in maternal and fetal tissues. The aim is to create an actionable roadmap for the early-life risks of micro- and nanoplastics. In this project, we work together with several other European universities, who focus on the toxicological and epidemiological viewpoints of micro- and nanoplastic health risk assessment, while I focus on the in-depth qualitative characterization of their morphology and chemistry. I combine several characterization techniques, such as IR, AFM, DLS, GCMS, to yield as much information as possible about these samples. First, some lab degradations will be needed before moving on to actual biological samples. A big challenge of my project will be to detect nanoplastics in biological material, which is very new to the ICC group. How to filter out biological material without removing micro- and nanoplastics from the samples will be challenging, especially since the morphology of micro- and nanoplastics is so divergent.

This project will gain insight into the pathways of micro- and nanoplastics formation and their possible health effects for fetuses. By working together with different universities all with their own expertise, we will be able to investigate the implications for human health of this world-wide problem and to help creating actionable tools for policy makers.

Understanding physicochemical processes on catalyst model systems using surface-sensitive characterization methods



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Supervisors: Prof. dr. ir. Bert Weckhuysen

Atomic force microscopy, In-situ, Nano-IR, Heterogeneous catalysis

Since heterogeneous catalysis involves processes on the solid/air or solid/liquid interface, it is important to utilize surface-sensitive characterization methods with a spatial resolution down to the nanometer region. In this manner, it becomes possible to understand the elemental distribution, the influence of morphology and the function of active sites. In this project, Scanning Probe Microscopy (SPM) methods are deployed to understand growth processes, catalytic activity as well as the stability of catalytic materials from a fundamental point of view. As an example, in-situ measurements using liquid-phase Atomic Force Microscopy (AFM) are performed on the nucleation and growth of a HKUST-1 thin-film, a Cu-based Metal-Organic Framework (Fig 1a).[1] The stability of such materials was tested using an autoclave-inserted AFM.[2] Both microscopic approaches were complemented using spectroscopic tools. Spectroscopic fingerprints can even be obtained with spatial resolution using AFM-IR, where a traditional detection system is replaced by AFM-tip based mechanisms (Fig 1b).[3] This leads to maps of specific vibrations with nanometer resolution. Complemented by Time-of-Flight SIMS (Fig 1c) and Kelvin Probe Microscopy (KPM), we can obtain a morphological and elemental “passport” of our model systems before, after or even during synthesis or catalytic processes. In the remainder of this research, this toolbox will be applied to study MOF catalysts, zeolite single crystals and films and bio-based membranes, such as chitosan.[4]

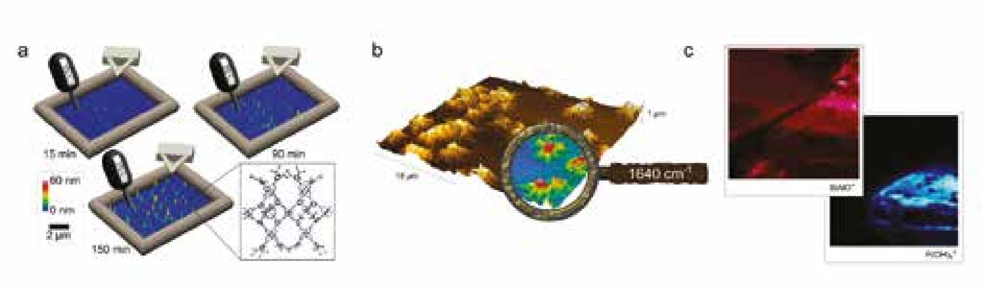
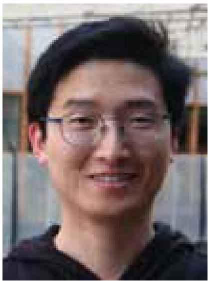


Figure 1: a) In-situ liquid AFM measurements on HKUST1 thin-film nucleation and growth. b) MOF thin-film with Nano-IR “hourglass” showing IR intensity c) Mass images of SiAlO+ and P(OH)4+ fragments on a zeolite surface after phosphatation, obtained using ToF-SIMS.

[1] L. D. B. Mandemaker, *et al.*, *J. Phys. Chem. Lett.* **2018**, 9, 1838-1844.
[2] R. P. Brand, *et al.*, *ChemPhysChem* **2018**, 19, 2397– 2404.
[3] G. Delen, *et al.*, *Chem. Eur. J.* **2018**, 24, 187 – 195.
[4] D. Fu, *et al.*, *Angew. Chem. Int. Ed.* **2018**, 57, 12458 –12462.

In situ X-ray diffraction studies for electrocatalysis: from electrode to single nanoparticle



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X-ray diffraction, Bragg Coherent Diffraction Imaging, electrocatalysis

Electrocatalysts play an important role in the transition towards a sustainable society. Nanomaterials are used as catalysts for a range of electrochemical reactions, and the activity and selectivity of nanocatalysts depend on many factors.[1] While extensive efforts have been devoted in optimizing electrode performance with high activity and selectivity, the poor stability of nanomaterials becomes a critical issue. The dynamic nature of nanoparticles under electrochemical conditions results in structural variations that determine the selectivity and activity on the single nanoparticle level. Therefore, thorough understanding of electrocatalysts requires both bulk electrode and single nanoparticle analysis.

In this work, we demonstrate a versatile in situ X-ray diffraction-based methodology which enables the structure and phase analysis of bulk electrodes and lattice strain analysis of single nanoparticles. A novel in situ electrochemical cell configured in back-illumination geometry has been fabricated to perform X-ray diffraction (XRD) and Bragg Coherent Diffraction Imaging (BCDI) with unfocused and focused beam respectively. In situ XRD has been collected during stepped cyclic voltammetry CO_2 saturated 0.1 M KHCO3 to trace the phase evolution of Cu electrode, while ex situ BCDI has been performed on single Cu nanoparticle in absence and presence of CO_2 saturated electrolyte. BCDI results demonstrate that that displacement appears mostly at the twin boundary and edges even without the presence of electrolyte. After introducing electrolyte, the displacement field at the twin boundary and the surface change significantly, which can be caused by adsorbed species or surface oxidation. With the strain and displacement field information, we observed the influence of electrolyte on the surface and boundary structure, which can help to identify the active sites and holds great promise for establishing the structure-performance relationship.

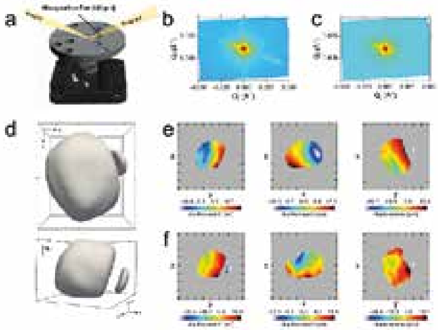

Figure 1: a. Schematic drawing of in situ electrochemical cell for X-ray diffraction studies. b, c. Measured diffraction intensity of Cu nanoparticle in absence (b) and presence (c) of CO_2 saturated 0.1 M KHCO3. d. Top isosurface view (top) of the reconstructed modulus. Side isosurface view (bottom) of the reconstructed modulus. The missing electron density corresponding to a part with a different crystallographic orientation (twin) is clearly visible. The tick spacing corresponds to 50 nm. e, f. 2D cross-sections of displacement field of Cu nanoparticle in absence (b) and presence (c) of CO_2 saturated 0.1 M KHCO3.

[1] R. A. Vicente, *et al.*, *ACS Nano* **15**, 6129-6146 (2021).

Multi-scale investigation of silica-supported ethylene polymerization catalysts during the early stages of the reaction

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Sponsor:	Dutch Polymer Institute (DPI), since May 2018
Supervisors:	Prof. dr. ir. Bert M. Weckhuysen, Dr. Florian Meirer

Polymerization catalysis, Micro-spectroscopy, X-ray nanotomography

The process of fragmentation (i.e., the breaking apart of the catalyst support due to polymer formation) has a critical influence on the morphology and activity of supported olefin polymerization catalyst particles.[1,2] In order to obtain more comprehensive insights into this phenomenon, **silica-supported metallocene-based and Ziegler-Natta catalysts** are investigated during the early stages of active site genesis and ethylene polymerization. Essentially, a multi-scale characterization approach, featuring advanced microscopy and spectroscopy techniques, is adopted. By doing so, properties of the above-mentioned catalyst materials can be obtained both at **the scale of the single polymerizing particle** (i.e., particle morphology, temperature gradients) and at the **atomic scale** (i.e., active site structure and accessibility).

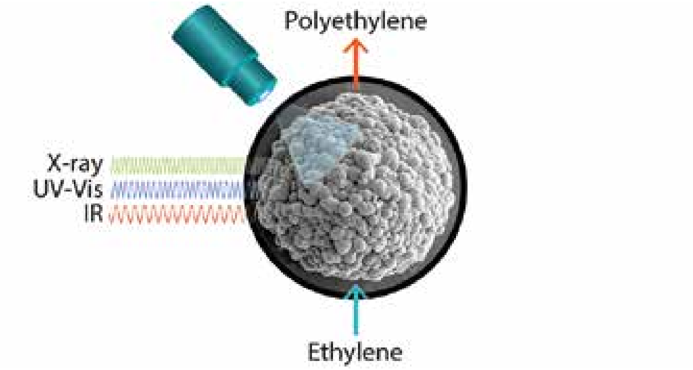

Figure 1: Schematic representation of our micro-spectroscopic approach.

Within this research project, we collaborate extensively with the group of Prof. Elena Groppo at the University of Torino (Italy), where bulk catalyst characterization is performed. Techniques such as UV-Vis spectroscopy, probe molecule infrared (IR) spectroscopy and X-ray absorption spectroscopy (XAS) have been employed to assess the structure and accessibility of the catalysts' active sites. Furthermore, sophisticated methods for the morphological characterization of individual catalyst particles have been developed. X-ray- and fluorescence-based tomography techniques (i.e., holotomography, nano computed tomography, confocal fluorescence microscopy) deliver 3D resolved morphological information on multiple catalyst particles at sub-micron spatial resolutions. Novel insights into the morphological evolution of these catalysts were hence obtained. By using thermoluminescent nanoparticles, we can also monitor the exothermicity of the polymerization reaction on our catalyst systems. This gives us insights into catalyst activity at the bulk and single particle level.

[1] J. R. Severn, *et al., Chem. Rev*. **2005**, 105, 4073–4147.

[2] J. B. P. Soares, *et al.*, *Polyolefin Reaction Engineering*, Wiley-VCH, Weinheim, Germany, **2012**.

Catalytically active coatings for the removal of indoor pollutants

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Photocatalysis, Supported metal oxides, Visible light

Nowadays, people spend roughly 90 percent of their time in indoors, such as in their homes or in the office.[1] Some people that spend large amounts of time in indoor environments report medical issues that have an unclear cause, but that might be related to poor indoor air quality. This is described as "sick building syndrome" and includes symptoms such as headaches, fatigue, and irritated skin and eyes.[2] Volatile organic compounds (VOCs) can decrease the air quality, even at very low concentrations in the parts per billion (ppb) range. This type of indoor air pollutant can be emitted *e.g.* from furniture, from consumer products and by cooking.[3] Photocatalytic oxidation is a promising technique that can break down the VOCs to water and carbon dioxide by means of reactive oxygen species (Figure 1). In this project, we aim to develop photocatalytically active materials that can degrade these indoor air pollutants using visible light. In addition to using sunlight, we will focus on the activation of the catalyst materials by modern indoor lighting (e.g. LED light including wavelengths in the near-UV region) varying in wavelength and intensity. The main photocatalysts that we will research are metal oxides supported on porous supports, such as zeolites and various amorphous supports. The most promising catalyst materials will be incorporated in paint systems, creating a functionalized paint which will be tested for its air purification activity. Advanced analytical methods in specially designed testing units for coating evaluation will be developed to detect various relevant target molecules at concentrations down to the ppb level.

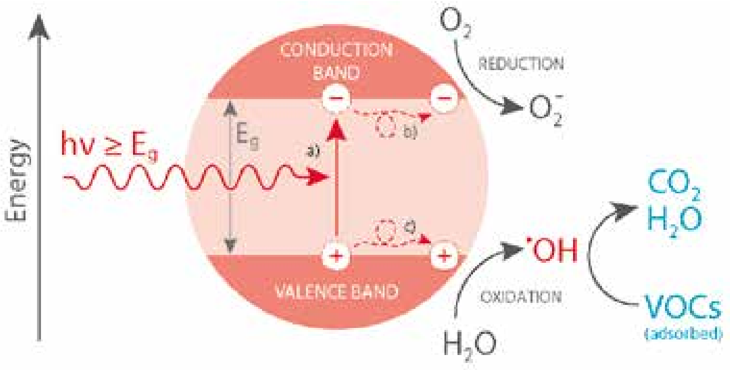

Figure 1: Free charges are created in a semiconductor photocatalyst particle by absorption of visible light (*hv*). Reactive oxygen species are then formed, which can oxidize the VOCs (adsorbed on the support material) to water and carbon dioxide.

[1] W. W. Nazaroff *et al.*, *Indoor Air* **25**, 357-361 (2015)

[2] D. Norbäck, *Curr. Opin. Allergy Clin. Immunol.* **9**, 55-59 (2009)

[3] S. Wang *et al.*, *Environ. Int.* **33**, 694-705 (2007)

Catalytic studies on co-processing of pyrolysis liquids and vacuum gasoil

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Bio-fuels, FCC catalyst, Deactivation

Biomass valorization draws great attention due to the depletion of carbon fossil resources and increased greenhouse gases.[1] Lignocellulosic biomass derived from industrial wastes and forestry can be an alternative feedstock for the production of second-generation biofuels. Liquids can be obtained from biomass by catalytic fast pyrolysis. However, pyrolysis liquids cannot be used as fuels directly due to their high oxygen content as they consist of oxygenated compounds (e.g., alcohols, phenol derivatives, and lignin-derived oligomers, etc.).[2] Further reducing the oxygen levels of pyrolysis bio-oils can be achieved by hydrodeoxygenation (HDO) over supported metal catalysts.[3] This process requires high temperatures and pressures as well as high amounts of hydrogen, which are important drawbacks. Co-refining pyrolysis liquids and vacuum gasoil in an existing FCC unit can be an alternative process for upgrading bio-oils.[4]

This project aims to understand and gain more insights into the co-fluid catalytic cracking of pyrolysis liquids in existing refineries. Focusing especially on:

- The development and the catalytic studies of improved FCC catalyst materials for oxygen-containing feeds
- The establishment of reaction pathways when a mixture of hydrocarbons and oxygenated compounds used
- The unravelling of the deactivation mechanism of FCC catalyst due to the partial substitution of vacuum gasoil with pyrolysis liquids.

[1] G.H. Huber, *et al., Chem. Rev.* **106** 4044–4098 (2006)
[2] M.C. Samolada, *et al., Fuel* **7** 1667–1675 (1998)
[3] J. Wildschut, *et al., Appl. Catal. B* **99** 298–306 (2010)
[4] N. Thegarid, *et al., Appl. Catal. B* **145** 161– 166 (2014)

Insights into CO_2 hydrogenation: tuning the selectivity by investigating multi-metal catalysts

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X-ray absorption spectroscopy, CO_2 valorization, Multi-metal catalysts

Converting the greenhouse gas CO_2 into chemicals and fuels constitutes a promising starting point to strive against the continuously increasing global CO_2 emissions and associated climate change. For thermocatalytic CO_2 hydrogenation towards methane, Ni-based catalysts are desired due to their high activity and selectivity. However, for value-added products besides methane, such as C_{2+}, the optimal catalyst is not yet found. To this end, Fe and Cu, as non-noble, abundant, and relatively inexpensive metals, constitute promising candidates, despite their significantly lower activity compared to Ni. A possible strategy to overcome the low activity, while taking advantage of their selectivity is a synergistic combination of Fe or Cu with Ni. Synergistically combining two metals represents an important strategy to tune the selectivity and activity of a catalytic reaction. For bimetallic catalysts, improved performance is frequently ascribed to metal alloy formation, although it is not yet well-understood how the two metals interact and boost the catalytic performance. Indispensable for unravelling the role of metal alloys in CO_2 hydrogenation are the appropriate characterization techniques. Especially for small nanoparticles, which lack long-range ordering, X-ray absorption spectroscopy (XAS) constitutes a powerful characterization tool, albeit its limited availability due to the necessity of precious beamtime at synchrotron facilities. However, the possibility to perform XAS nowadays also in the laboratory offers new opportunities for detailed catalyst characterization and presents an alternative and complement to studies at synchrotron facilities. In this project, a special emphasis lies on the advanced characterization of multi-metal CO_2 hydrogenation catalysts with laboratory- and synchrotron-based XAS. The overall goal is to improve the understanding of the crucial role of metal alloys in CO_2 hydrogenation and to unravel both metal and metal ratio dependent differences, i.e., varying alloy composition. Hereby, taking a step further towards targeted CO_2 valorization.

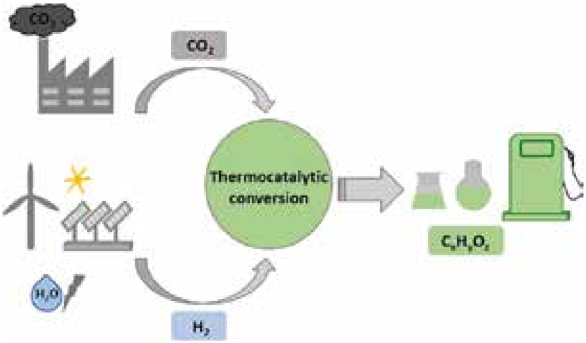
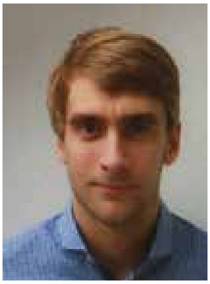


Figure 1: Scheme of the thermocatalytic conversion of CO_2 and H_2 in the context of producing sustainable chemicals and fuels

Exploring the complexity of pore space of a catalyst particle



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Supervisors: Prof. dr. ir. Bert M. Weckhuysen, Prof. dr. ir. Albert van den Berg, dr. Florian Meirer, dr. Mathieu Odijk

Mass transfer, Single particle tracking, Micro- and nanofluidics

Mass transport is a crucial aspect of catalytic performance, as it can influence the activity, selectivity and lifespan of a catalyst. Therefore, providing a better understanding of the molecular motion is of upmost importance to rationally design catalysts. Traditional diffusion experiments rely on bulk measurements, which ignore the heterogeneity of diffusant behavior caused by host-probe interactions [1]. One way to unravel these diffusion heterogeneities, is localizing fluorescent probes over time with super-resolution fluorescence microscopy leading to tracks (see figure 1 b). These can then be used to obtain information about the local pore geometry and composition as well as how these properties relate to the diffusion coefficient of individual probes. A former member of our group successfully tracked single fluorophores inside fluid catalytic cracking particles, shedding a light on the ensemble-free diffusion behavior under confinement [2]. However, the pore space of each catalyst is extremely complex and in many cases unknown, which heavily complicates relating tracks to local pore geometries and/or composition.

In order to tackle this problem, we chose a bottom-up approach in which single diffusants are traced over time in a well-defined model structure, where both composition and geometry are known. Therefore, we use silica nanofluidic devices (see Figure 1 a) fabricated with photolithography and wet etching as artificial pores. By tunning the probe-wall interactions (e.g. through pH variation) different diffusion and adsorption/desorption behaviors can be observed. The combination of these experimental results together with mass transfer simulations, will allow us to better understand how molecules move inside real catalysts.

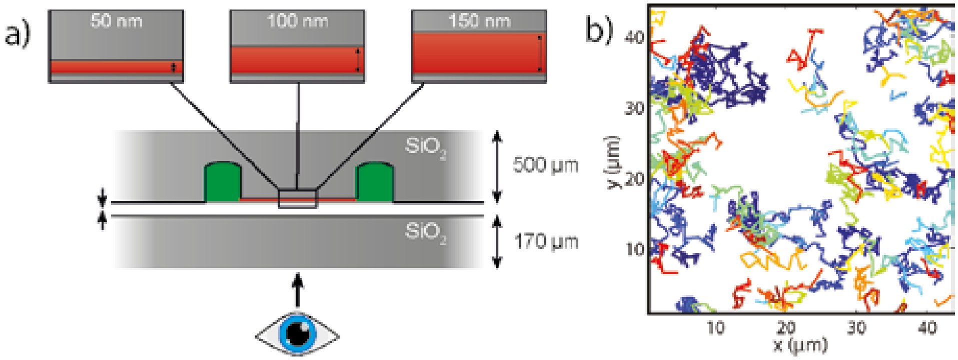

Figure 1: a) Schematic cross section of a microfluidic device showing the etched microchannels (green) and nanoslits (red). b) Overlay of tracks collected in a 100 nm deep nanoslit over 5 seconds (probe: CdSe-ZnS-PEG quantum dots)

[1] J. Kärger *et al. New J Chem.* **40**, 4027-4048 (2016)

[2] F. Hendriks , *J. Am. Chem. Soc.* , **139**, 13632–13635 (2017)

Time-gated raman spectroscopy of light alkane dehydrogenation catalysts

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dr. Freddy Rabouw

Time-gated raman spectroscopy, Propane dehydrogenation, Coke formation

Light olefins, such as propylene and ethylene are key building blocks in the chemical industry for the production of polymers, oxygenates and other chemical intermediates. Dehydrogenation of propane, facilitated by either platinum-tin or chromium oxide based catalysts is a major industrial road towards propylene. Coking and subsequent activity loss of the catalyst occurs during this process as the products of side reactions react with the olefin. The catalytic activity is regained in an oxidative regeneration step.[1]

Operando Raman spectroscopy has been used in this group to investigate the dynamics taking place within a dehydrogenation catalyst. Unfortunately, a strong fluorescence background overshadowed the Raman scattering during initial stages of hydrogenation and regeneration.[2] Raman scattering and fluorescence occur on a different timescale and can therefore be separated by measuring in a time-resolved manner with the aid of new commercial time-gated Raman spectroscopy instruments.

The aim of this project is to develop and explore time-gated Raman spectroscopy to gain more understanding in coke formation during successive dehydrogenation and regeneration cycles under industrial relevant conditions. In a second step, we strive to use shell-isolated nanoparticles enhanced Raman spectroscopy (SHINERS) to further increase the sensitivity of the Raman technique. The combined information obtained from both techniques offers direct means to define protocols for optimal regeneration of dehydrogenation catalysts.

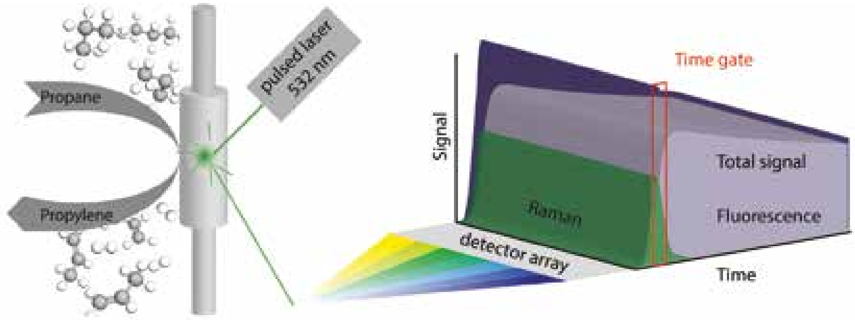

Figure 1: Schematic representation of propane dehydrogenation studied with time-gated Raman spectroscopy.

[1] J.J.H.B. Sattler *et al.*, *Chem. Rev.* **114**, 10613-10653 (2014)

[2] J.J.H.B. Sattler *et al.*, *Phys. Chem. Chem. Phys.* **15**, 12095–12103 (2013)

Development of catalytically active b-oriented ZSM-5 membranes

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Zeolite, Membrane, Catalysis

Recently, research interest into the synthesis of b-oriented ZSM-5 zeolite membranes has picked up significantly. Thanks to their catalytic activity and separation functionality these membranes have a promising future in industrial processes that involve catalytic membrane reactors. In addition, the specifically controlled orientation of the microporous channels will enhance molecular diffusion properties of the zeolite.
In the first part of this project we develop facile synthesis methods that result in robust, well-intergrown *b*-oriented membranes. In the past year a less corrosive, neutral growth medium was developed by varying synthesis conditions and additives (Fig. 1). In the second part of this project, these membranes are further optimized to be used in various catalytic applications. As a part of this phase, a reactor will be developed to demonstrate the membranes in industrially relevant applications.

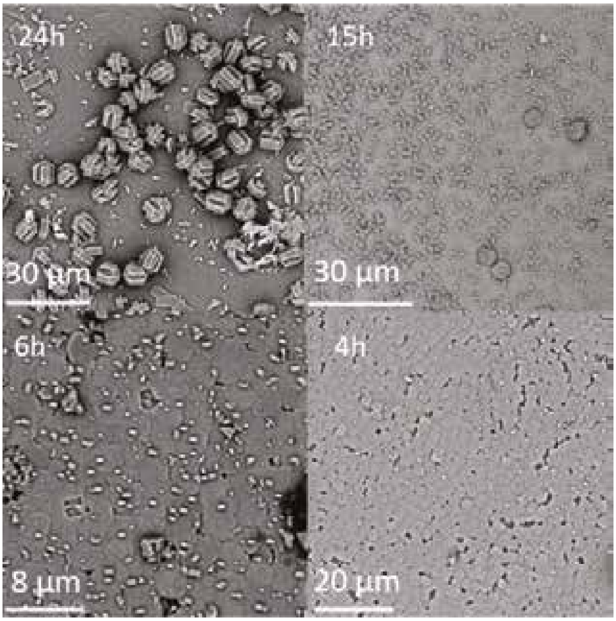

Figure. 1: The formation of oriented membranes as a function of synthesis conditions at pH = 8.

Pyrolytic upgrading of methane to aromatics

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Methane activation, Operando spectroscopy, Catalytic activity testing

Methane is a cheap and abundant carbon feedstock which has the potential to become the source for lower olefins and aromatics in an atom- and energy-efficient way.[1] The Methane dehydroaromatization (MDA) reaction is especially suitable for this task, as methane transformation is achieved without any oxidants, resulting in excluding the greenhouse gas CO_2 as a reaction product and instead producing hydrogen.[2] Unfortunately, the catalyst (usually Mo/ZSM-5) for the MDA reaction suffers from rapid deactivation due to coking.[3] Fundamental insights into this process, e.g. the identification of the coking site, or the mechanism of coke formation are still missing which hinders the development of new more coke-resistant catalysts. In my project I aim to utilize and develop various operando techniques to gain a better understanding of the working catalyst (Figure 1 left). In the course of this project I plan to expand the set of investigated catalysts from the mostly used Mo/ZSM-5 catalyst to W/ZSM-5 and Fe/ZSM-5 which were shown to also have MDA activity.[4] Unfortunately, only few methods currently exist that can observe methane radicals, an hypothesized intermediate of methane activation, during the reaction. One possible method is planar laser induced fluorescence (PLIF) where a laser is used to excite a pre-determined probe molecule. After the excitation the molecule returns to its ground state through fluorescence, which can be detected. We envisioned a setup where a thin-film catalyst is exposed to the reaction conditions in a spectroscopic cell and a laser film is shot above the catalyst's surface (Figure 1 right). This enables us to study the gas phase independently of what is happening inside the catalyst's pores.

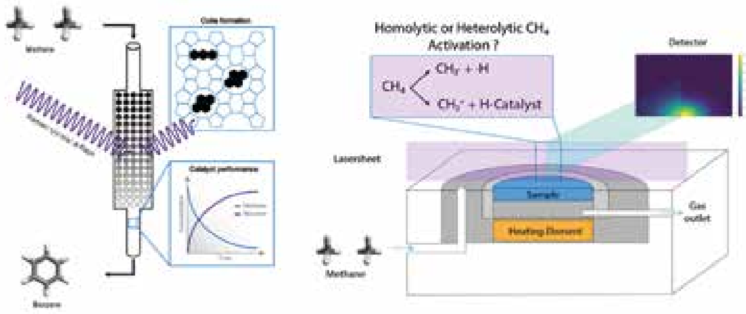

Figure 1: Left: Using *in-situ/operando* spectroscopy to investigate coke formation. Right: Using in-situ spectroscopy (e.g. Planar Laser Induced Fluorescence, PLIF) to investigate gas phase.

[1] BP p.l.c., *BP Statistical Review of World Energy* 2018 (2018)

[2] E. T.C. Vogt *et al.*, *Adv. in Catal.* **58**, 143-314 (2015)

[3] I. Vollmer *et al.*, *ChemCatChem* **11**, 39-52 (2018)

[4] B. M. Weckhuysen *et al.*, *J. Catal.* **175**, 338-346 (1998)

Value-added products from polyolefin waste by catalytic pyrolysis

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Sponsor: MCEC, since June 2021
Supervisors: prof. dr. ir. Bert Weckhuysen, dr. Ina Vollmer

Catalysis, Plastics, Pyrolysis

Due to insufficient recycling and incineration, plastic waste has become a global problem. In my research, I'm trying to find economically viable ways to convert polyolefin waste to value added products, be it chemicals, fuels, or cracker feed. The process of choice is catalytic pyrolysis, during which the plastic is heated together with a catalyst to high temperatures under inert atmosphere. I'm trying to understand how different catalyst properties affect the product distribution, to be able to design a catalyst that allows to convert plastic waste into something of significantly increased value. Beside my experimental work, I'm also highly interested in applying new DFT tools to fundamentally enhance our understanding of heterogeneously catalyzed processes.

Structure-performance relationship over Cu-based catalysts in electrochemical CO_2 conversion

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Sponsor:	EU Framework Programme, since August 2019
Supervisors:	prof. dr. ir. Bert Weckhuysen, dr. Ward van der Stam

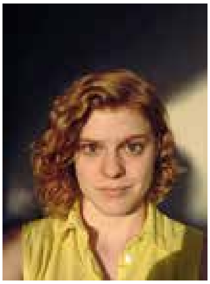
Electrochemistry, bimetallic, copper

Electrochemical CO_2 reduction reaction (CO_2RR) represents a promising approach towards artificial carbon recycling for addressing global challenges in energy and sustainability. For this process, Cu is the only metal known to catalyze the CO_2RR to hydrocarbons with adequate efficiency, but it suffers from poor selectivity. Among a variety of factors that impact CO_2RR selectivity and activity (including catalyst morphology, composition, pH and ions in an electrolyte, reactor design), catalyst surface structure attracts a lot of attention due to its importance for essential mechanism study and rational design of advanced electrocatalyst. Significant breakthroughs are often the result of deeper understandings of the relationship between surface structures and catalytic performance. In this project, the design and synthesis of Cu-based nano-catalysts capable of producing selective products with high activity will be systematically developed by electrodeposition and wet chemical method for example. As for mechanism investigation, advanced operando X-ray techniques (XAFS, GIXAS) will be used for identifying catalytically active sites and structure evolution of as-prepared catalysts during reaction. Optical techniques (Raman and FTIR) are also of interest for key intermediate and reaction pathway identifications.

[1] S. Nitopi, *et al., Chem. Rev.* **119**, 7610-7672 (2019).

[2] D.Gao, *et al., Nat. Catal.* **2**, 198–210 (2019).

Analysis of catalyst for electrochemical alcohol oxidation coupled to hydrogen production



Sibylle Schwartmann, s.m.k.schwartmann@uu.nl
Sponsor: None, Since June 2021
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Electrochemistry, Alcohol oxidation, Hydrogen production

Hydrogen production via the electrochemical splitting of water is limited by the evolution of oxygen at the anode. Oxygen as a product is not much needed, and the OER is kinetically slow and needs a large overpotential. Therefore, alternative anodic reactions are researched which can produce valuable base chemicals while kinetically beating the OER. My research focuses on analyzing promising catalysts for these reactions starting with the oxidation of propanol as an example reaction.

Operando micro-spectroscopy of coke formation in methane dry reforming catalysis

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Sponsor: BASF, since March 2021
Supervisors: prof. dr. ir. Bert M. Weckhuysen, dr. Ward van der Stam
dr. Matteo Monai

Methane dry reforming, Catalyst deactivation, Operando spectroscopy

The project is a collaboration between ARC CBBC and BASF, and focusses on dry reforming of methane (DRM), in which greenhouse gases CH_4 and CO_2 are converted into synthesis gas (mixture of CO and H2). Synthesis gas can be readily transformed into numerous value-added chemicals and fuels. However, high temperatures (800-1200 °C) are required to perform the DRM reaction, which places severe challenges on the catalyst employed, which are usually Ni-based catalysts. They often suffer from rapid deactivation due to carbon deposition and particle sintering. Therefore, many efforts are directed toward the design and preparation of more stable DRM catalysts.

The aim of this project is to provide useful structure-performance relationships and to gain new insights into the deactivation mechanism of Ni-based catalysts in the DRM reaction. This will be done by using *operando* Raman spectroscopy, which will give information on the amount and speciation of the carbon deposition during the reaction. The degree of carbon deposition will be correlated with structural and chemical changes of the catalyst, which can determined with operando X-ray diffraction as well as X-ray absorption spectroscopy (XAS). The new insights obtained will aid in better catalysts synthesis by rational catalyst design.

Exploration of non-commodity zeolite frameworks for small molecule activation: acidity, reactivity and coke formation

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Sponsor:	BASF/ARC CBBC, since February 2018
Supervisors:	prof. dr. ir. Bert Weckhuysen

Zeolites, Operando spectroscopy, Atom probe tomography

Zeolites are widely used solid catalysts in various applications, including chemical industry. Although there are more than 235 zeolite frameworks reported, almost all zeolite-based catalytic processes are performed by a limited number of frameworks. These are the so-called Big Five: FAU, MFI, FER, MOR and BEA. More recently, SAPO-34 and SSZ-13 with the CHA structure became important catalysts in e.g. methanol-to-hydrocarbon (MTH) process and selective catalytic reduction of NOx.

Since industry wishes to develop more sustainable conversion processes, it is crucial to explore the properties of less conventional zeolite frameworks. In this research project, several non-commodity zeolite framework structures are investigated as examples of small molecule activation processes. To gather detailed physicochemical insights of these materials, a wide variety of bulk and local characterization methods will be used, while their performance is studied in the methanol-to-olefins (MTO) process as showcase. The latter allows making comparisons with current MTO catalysts. The catalytic properties under working conditions are investigated with operando spectroscopic techniques (UV-vis/XRD). Additionally, atom probe tomography (APT) will be used as a key tool, since detailed information can be obtained about the 3D spatial composition of the framework elements and the coke molecules formed during the MTH reaction. Figure 1 represents a schematic overview of the APT working principle and the atom maps obtained with this technique.

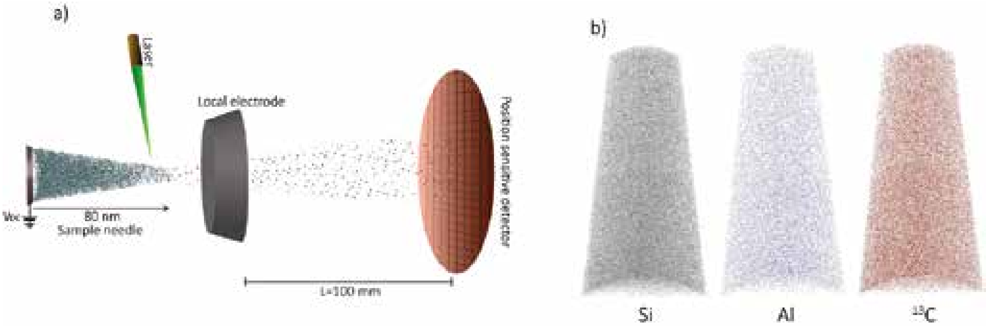

Figure 1: a) Schematic representation of the working principle of atom probe tomography (APT); and b) reconstructed atom maps with APT.

Detection and exploiting local phenomena in catalytic CO_2 conversion

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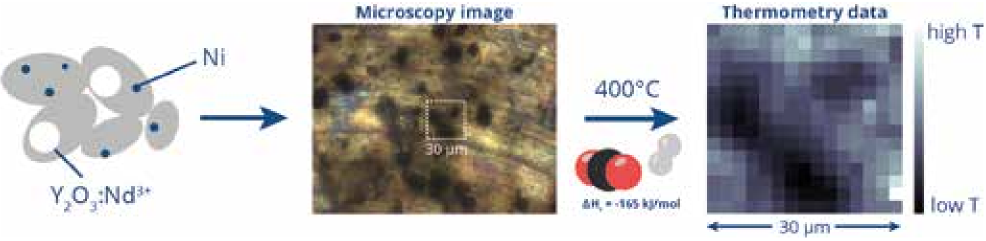
Sponsor:	Tata Steel, NWO and M2i, since September 2020
Supervisors:	dr. Ward van der Stam, prof. dr. ir. Bert Weckhuysen

Luminescence thermometry, Shell-isolated nanoparticle enhanced raman spectroscopy, CO_2 Valorization

One of the largest CO_2 emitting industries is the metallurgical industry, including steel producers. Tata Steel recently developed a new process, called HIsarna, in which the CO_2 emissions are reduced by at least 20%. [1] The works arising gases (WAGs) of the HIsarna process are CO_2-rich (almost 70% CO_2) and high in temperature (up to 1500°C). The overall project aims to develop the necessary thermo- and electrocatalysts to convert these WAGs into valuable chemical building blocks, using the high temperature of the HIsarna WAGs.

Within this project, analytical tools are required to monitor the CO_2 conversion. By designing bifunctional electrodes, containing the catalyst, shell-isolated nanoparticles (SHINs) and temperature probes, local adsorbates and heat effects can be studied. These local sensors enable a direct comparison between the electrochemical and thermochemical conversion routes, where the mechanistic pathways of the CO_2 conversion can be investigated on catalysts without intrinsic SERS activity. Since the electrochemical conversion is performed at temperatures of up to 200°C, local heat effects can play a crucial role. Thermometry will be used to study these local heat effects, for example the effect of the current density on the local temperature.

Combining shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) and luminescence thermometry at the same time for *operando* monitoring of catalysis has already been studied within our group, but was limited to temperatures of ~350°C. [2] The main challenge for this project is therefore to find the optimal thermometry probes and SHINs for the designated reaction conditions, since the second step in the thermocatalytic CO_2 conversion requires temperatures of up to 800°C. [3] The deployment of these analytical techniques at high temperatures enables a more detailed study of the CO_2 conversion and can contribute to an even further decrease in CO_2 emissions from the steel industry.



[1] A. Keys, *et al.*, Decarbonisation options for the Dutch Steel Industry (2019).

[2] T. Hartman *et al.*, *Nat. Catal.* **2**, 986–996 (2019).

[3] I. Vollmer *et al.*, *ChemCatChem* **11**, 39-52 (2019).

Shell-isolated nanoparticle-enhanced raman spectroscopy for heterogeneous catalysis

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Supervisors: prof. dr. ir. Bert M. Weckhuysen

Raman spectroscopy, Nanoparticles, Illustrations

I am working with gold and silver nanoparticles to enhance Raman signals (Figure 1a) with factors up to 10^6. This technique is called surface-enhanced Raman spectroscopy (SERS) and is useful for the detection of low concentrated molecules, such as the detection of trace molecules, even single molecules or in this work: adsorbed molecules during catalysis. The primary reason for the local enhancement of the Raman signal in SERS is predominantly ascribed to the special optical properties of gold and silver nanoparticles. These noble metal nanostructures can focus light within a few nm of their surfaces due to the collective resonant oscillation of free surface electrons upon excitation with light, which is referred to as localized surface plasmon resonance (LSPR, Figure 1b). This strong enhancement and its highly local area of effect give both great opportunities and challenges to overcome, which we are investigating at ICC.

Two of such challenges are the application of the nanoparticles at more severe catalytic conditions while keeping the technique non-invasive or inert. Using shell-isolated nanoparticles, such as Au@SiO_2 (Figure 1c), we can now perform operando experiments with temperatures up to 400 °C at various pressures in oxidative and reductive environments, and we are exploring options on how we can further improve this range. Another challenge is the understanding of the positioning of so-called hot spots: where the local field enhancements are significantly stronger than average (Figure 1c). We would like to know where these hot spots are located so we can better understand what we are measuring and how we can improve our nanostructures.

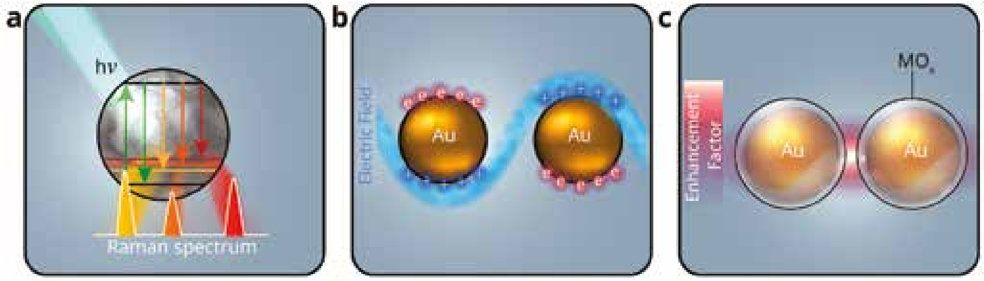


Figure 1: a) Raman spectroscopy, light excites the material to a virtual state and directly scatters Rayleigh scattering and Stokes-shifted Raman scattering, resulting in a spectrum. b) Electric field results in the polarization of gold nanoparticles. c) Two (or more) shell-isolated nanoparticles can couple their plasmon resonance, resulting in even stronger local field enhancements at the hot spots.

Structural evolution and dynamics of an In_2O_3 catalyst for CO_2 hydrogenation to methanol

Xian Wu, x.wu3@uu.nl
Sponsor: China Scholarship Council, since Nov. 2020
Supervisors: prof. Bert M. Weckhuysen, dr. Ward van der Stam
dr. Matteo Monai

In_2O_3 Catalyst, CO_2 Hydrogenation, Methanol

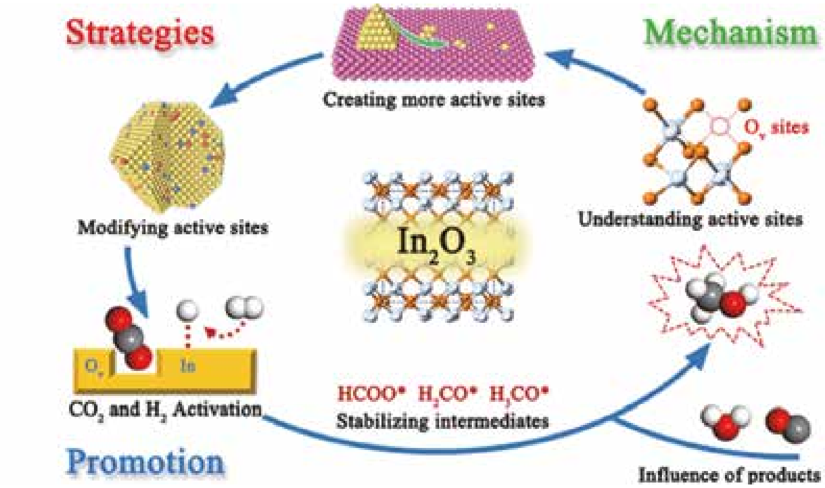
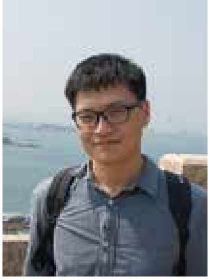


Figure 1: CO_2 hydrogenation to methanol over In_2O_3-based catalysts: from mechanism to catalyst development.[1]

[1] J. Wang *et al.*, *ACS Catal.* **11**, 1406–1423 (2021)

Alumina-based single atom catalysts for the activation of methane



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Sponsor: China scholarship Council, since November 2019
Supervisors: prof. dr. ir. Bert Weckhuysen, dr. Matteo Monai

Single-atom catalyst, Methane activation, Operando spectroscopy

The goals of my research are to establish high performing single-atom catalyst systems for the selective conversion of methane, and to obtain the fundamental insights into the catalytic mechanism and the dynamic change course of a working single-atom catalyst, with the assistance of operando spectroscopic techniques and ab-initio simulation methods.

In-depth investigation of porous catalysts, relating their complex pore space to catalyst performance

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Sponsor: UU-NWO, since March 2020
Supervisors: Dr. Florian Meirer, prof. dr. ir. Bert Weckhuysen

Fluorophore, Heterogenous catalyst, Mapping

In order to understand the catalytic performance of specific materials, it is essential to know the different sites of a heterogeneous catalyst. The objective of this project is to use super-resolution optical microscopy techniques (for example, single-molecule fluorescence microscopy) to discern the accessibility, distribution, and types of different sites on nano-porous solids and catalysts. We are developing new chemo-sensitive organic/inorganic luminescence materials (e.g., carbon dots) as probes of specific sites in solid materials to achieve this goal. Additionally, we are also preparing a well-defined model system (e.g. hierarchical mesoporous zeolite crystals, Fig. 1a) to study emission of the fluorophores on the surfaces/in proximity of different materials. Using the developed approaches, we will be able to map the 3D properties (e.g. acidity and hydrophobicity) of nanoporous particles with submicron resolution. Fig.1b shows the preliminary results obtained after staining by developed fluorophores.

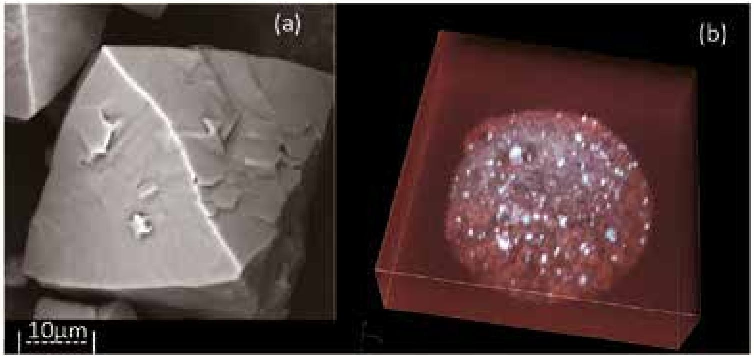

Figure 1: a) SEM image of a micron sized Y zeolite crystals prepared as model system, b) 3D construction of confocal microscopy image of an industrial catalyst particle (FCC catalyst) after staining by developed fluorophores.

Towards understanding the selective hydrogenation of nitriles to primary amines over modified raney nickel catalysts

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Sponsor: DSM, since May 2019
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Infrared spectroscopy, Nitrile hydrogenation, Catalysis

Nitriles are important precursors for the production of amines, chemical buildings blocks used in plastics, pharmaceuticals and agriculture. Although the hydrogenation reaction from nitriles to primary amines is straightforward, the subsequent condensation reaction towards secondary amines and imines results in loss of selectivity. The industrially relevant selective hydrogenation of nitriles towards primary amines can be steered by altering the catalyst with modifying agents or by adding supplements to the reaction, however, this process is still poorly understood.

In this project I would like to investigate the mechanism of the subsequent condensation reaction and the interaction between the catalyst and modifying agents using various in-situ and operando spectroscopy techniques such as FT-IR, Raman and UV-Vis spectroscopy combined with ex situ techniques such as high-performance liquid chromatography (HPLC), scanning electron microscopy (SEM), X-ray absorption spectroscopy (XAS), temperature programmed desorption (TPD) and nuclear magnetic resonance (NMR) spectroscopy. The insight obtained in the combined studies will be used to further improve the existing catalyst modification and design new catalysts specifically for this reaction. The new catalyst materials could improve the overall selectivity of the reaction and the efficiency of a process widely used in industry.

Metal-organic framework thin films for ethylene polymerization

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Sponsor: DICP, since March 2020
Supervisors: prof. dr. ir. Bert Weckhuysen

MOF thin films, Ethylene polymerization

My research focuses on MOF thin films as 2D model catalysts for ethylene polymerization. Due to the wide range of possible uses, over 80 million tons of poly(ethene), is manufactured each year making it the world's most important polymer. Nowadays, polyethylene production mainly revolves around three catalysts, Phillips, Ziegler–Natta and metallocenes.[1] With these catalysts, a variety of PE are produced with required physicochemical properties.[2] However, the discovery and development of new catalysts for ethylene polymerization keeps driving worldwide research efforts. Metal-organic frameworks (MOFs) are organic-inorganic hybrid solids with uniform framework structures built from organic linkers and inorganic metal nodes. Due to the inherent diversity, the tunable porosity, and functionality, MOFs materials have also received a lot of attention as catalysts.[3] MOF thin films not only share some of the relevant features of bulk MOF crystals but also offer additional advantages in catalytic reactions. By growing MOFs as thin films, additional properties and potential applications become available. It may also provide us new insights into ethylene polymerization by applying MOF thin films as model catalyst.

[1] J. R. Severn *et al.*, *Chem. Rev.* **105**, 4073-4147 (2005)
[2] M. Rivera-Torrente *et al.*, *ACS Catal.* **9**, 3059-3069 (2019)
[3] Q. Wang *et al.*, *Chem. Rev.* **120**, 1438-1511 (2020)

4

MATERIALS CHEMISTRY AND CATALYSIS

Scientific staff	prof. dr. Petra de Jongh, prof. dr Frank de Groot, prof. dr. ir. Krijn de Jong (em), dr. Peter Ngene, dr. Jessi van der Hoeven, dr. Nong Artrith
Technical support	Ad van der Eerden, Dennie Wezendonk, Jan Willem de Rijk, Hans Meeldijk, Remco Dalebout
Administrative staff	Ilonka Buhrs, Sylvia Visser
PhD students/Postdocs	25

Research Mission

Our group focuses on the synthesis, characterisation and performance of heterogeneous catalysts. These allow efficient chemical conversions (and hence decrease the use of energy and raw materials), but are also essential to allow the transformation from fossil to renewable fuels. With fundamental research we unravel structure-performance relationships, but we also investigate large scale existing industrial processes (methanol synthesis, Fischer Tropsch synthesis, hydroisomerisation, ammonia synthesis, epoxidation and other selective hydrogenation and oxidation reactions in both gas and liquid phase).

We are also very active in the field of energy materials: for instance to produce electrocatalytically fuels from CO_2 *and* H_2*, reversible hydrogen storage, and next generation battery materials. We lead the materials research line in RELEASE, the national consortium to enable large scale reversible energy storage. Another stronghold is the characterisation of these complex materials with advanced (in-situ and operando) spectroscopic and microscopic techniques, most notably advanced X-Ray absorption spectroscopy and transmission electron microscopy. Next to this the groups avails of an impressive experimental infrastructure for the synthesis, characterisation and testing of catalysts and energy materials.*

Ultra-pure and structured supports for silver catalysts for ethylene epoxidation

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Sponsor: Industry/ARC CBBC, since March 2021
Supervisor: prof. dr. Petra de Jongh

Silver catalyst, Macroporous support, Ethylene epoxidation

In this project we will explore new approaches to design and assemble high surface area metal oxide nanostructures, with high phase and surface purity. These serve as supports for model catalysts that will be tested in industrially relevant reactions to provide insight on the role of the support, which is useful to optimize existing catalysts. Examples of possible design routes for structured supports are the use of replicas, sacrificial templates (such as stacked PMMA spheres), or direct foaming techniques.[1],[2]

A first model reaction that we study is the epoxidation of ethylene, which is very sensitive to impurities, promoters, and non-uniformities, and is highly relevant for industry: with an annual ethylene oxide production of circa 35 Mton [3], ethylene epoxidation is one of the largest industrial processes worldwide. The formation of ethylene epoxide by mild oxidation of ethylene is catalysed by silver particles deposited on an α-alumina support. Industrial catalysts show selectivities of around 90%, but only at low conversions. The unwanted side reaction is the complete combustion of ethylene to CO_2.

For these epoxidation catalysts, the support has a large influence on catalyst stability and selectivity towards the desired product. α-Al_2O_3 is used as commercial support for ethylene epoxidation catalysts, because it displays a low volumetric density of surface OH groups, due to both a low OH surface group density and a low specific surface area. The OH groups facilitate the unwanted side-reaction of ethylene oxide to eventually CO_2.[4] While α-alumina reduces side reactions, its low surface area is disadvantageous for the stability of silver particles. Building on our ultra-pure supports with controlled structure, we aim to gain a better understanding of the influence of support, impurities and promoters on the selectivity and stability of these catalysts. Other industrially relevant model reactions will be considered at a later stage of the project.

[1] A. R. Studart *et al., J. Am. Ceram. Soc.* **89**, 1771-1789 (2006)
[2] J. E. van den Reijen & P. H. Keijzer, *Materialia* **4**, 423 – 430 (2018)
[3] J. E. van den Reijen *et al., Catal. Today* **338**, 31-39 (2019)
[4] M. O. Özbek & R. A. van Santen, *Catal.* **143**, 131-141 (2013)

Electrocatalytic reduction of carbon dioxide: elucidating the role of silver nanostructures and the carbon support

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Supervisors: prof. dr. Petra de Jongh, dr. Peter Ngene

Silver nanostructure, Carbon support, Electrocatalysis

Anthropogenic carbon dioxide (CO_2) emissions are the major cause of climate change. To mitigate the effect of climate change, the share of renewable energy increased over the past decades. The electrocatalytic reduction of CO_2 is an interesting prospect to convert a greenhouse gas to valuable chemicals by using renewable electricity as the energy input. In this pioneering work, Hori showed that silver-based electrocatalysts were highly selective towards CO, which can be utilized with H_2 (syngas) to produce hydrocarbons.[1] [2] Therefore, many research groups focused their attention on the development of nanostructured silver catalysts supported on conductive substrates.[3][4]

The goal of my PhD project is to study the electrocatalytic conversion of CO_2 into value-added chemicals, such as carbon monoxide, by synthesizing, characterizing and testing carbon supported silver nanostructures (figure 1). In particular, the aim is to fundamentally understand the effect of different silver morphologies, such as nanoparticles and nanowires, and carbon surface functional groups on the activity and selectivity towards CO_2 electroreduction products. In a broader prospective, the fundamental insight gained in this work will facilitate rational electrode design for CO_2 electrochemical reduction and syngas applications.

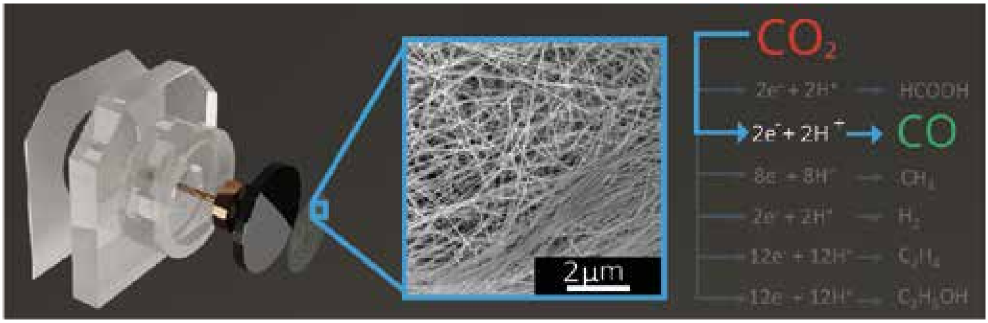

Figure 1: Working electrode configuration with carbon electrode covered with silver nanowires (left). SEM image of silver nanowires (center). CO_2 electrochemical reduction to CO (H_2O by-product is not shown) (right).

[1] Y. Hori *et al., J. Phys. Chem. B.*, **101**, 7075–7081 (1997).
[2] P. de Luna *et al., Science*, **364**, 350-359 (2019).
[3] M. Ma *et al., Angew. Chemie*, **55**, 9748-9752 (2016).
[4] N. J. Firet *et al., Catal. Sci. Technol.*, **10**, 5870-5885 (2020).

Supported copper nanoparticles for selective hydrogenation

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Sponsor: NWO VICI
Supervisors: prof. dr. Petra de Jongh, dr. Laurent Delannoy

Copper nanoparticles, Hydrogenation catalysts, Support and co-promoter effects

Hydrogenation reactions play a crucial role in fine chemicals production, as well as in purification processes. Notable examples are the removal (via reduction) of unwanted alkadienes/alkynes impurities from mono-unsaturated streams and synthesis of mono-unsaturated pharmaceutical intermediates.[1] All these processes require particularly high selectivities, since all the species in the gas or liquid mixture can potentially be hydrogenated. These requirements are usually achieved by means of expensive and complex hydrogenation catalysts, such as partially poisoned or modified Pd and Pt based systems.[1]

In the last decades, copper nanoparticles appeared to be a valuable alternative to noble metal hydrogenation catalysts. They are easy to manufacture, inexpensive and already proven to be selective in other industrially relevant hydrogenation, such as in methanol synthesis. Nonetheless, little is known about the parameters that determine the Cu catalytic performance in the conversion of polyunsaturated compounds.

The goal of this project is to investigate the catalytic properties of differently sized Cu nanoparticles (2-10 nm) immobilized on either silica gel or carbon supports, with and without the presence of stability/selectivity promotors. The catalysts are tested in both gas and liquid phase hydrogenation reactions. Rigorous kinetic modeling and hydrocarbon adsorption experiments are used in order to infer about the role of different active centers and activity/selectivity-structure relationship. Initial results from this project have already shown that finely tuned Cu nanoparticles on SiO_2 are able to retain their initial activity for 60h on stream in the selective hydrogenation of traces amount of 1,3-butadiene (3000 ppm) in a 30% propene/He gas mixture.[2] In addition, their selectivity to butene was nearly full (>99%) thanks to the ability of the Cu nanoparticles active centers to adsorb 1,3-butadiene more strongly than propene.[2]

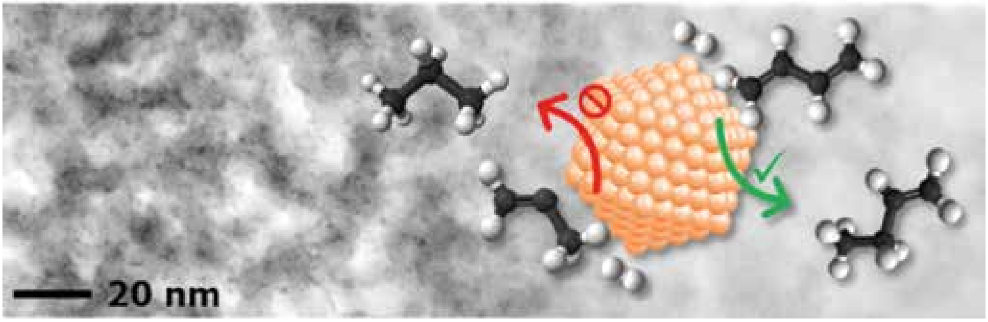

Figure 1: Artistic representation of the selective hydrogenation of 1,3-butadiene in presence of propylene over a Cu NP. In the background: 2nm Cu particles on silica, obtained via IWI technique.

[1] G. Bond, Metal-catalysed reactions of hydrocarbons, *Springler* (2005).
[2] G. Totarella *et al.*, *J. Phys. Chem. C*, **125** 366-375 (2020).

Developing high-performance solid-state anion conductors

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Sponsor: UU, since October 2020
Supervisors: dr. Peter Ngene, prof. dr. Petra de Jongh

Solid electrolytes, Anion conductors, Batteries

For the development of the next generation of batteries, many researchers have turned to solid-state electrolytes/ion conductors because they can enable safer and high energy density batteries.[1] Solid electrolytes are inorganic or polymer-based solids in which ions move freely within the material. Lithium and sodium ion conductors have received particularly much attention as they are crucial for high capacity and low cost batteries based on lithium and sodium metals. Many different types of solid electrolytes have been developed in recent times.[1] Although the focus has mostly been on materials in which the cations are the mobile ion of interest, solids in which anions (such as H^-, OH^-, O^{2-}, F^- and Cl^-) are highly mobile, are also interesting for a variety of electrochemical processes such as batteries, fuel cells, electrolysis, chemical sensors and catalysis. Unfortunately, most of the currently known solid-state anion conductors show high conductivity only at elevated temperatures.

The focus of my work is on the development of novel solid-state anion conductors, in particular hydride, hydroxyl, and halide ion conductors, with high ionic conductivity at moderate temperatures. The goal is to investigate how strategies such as ion substitution, nanoconfinement and interface engineering can be used to increase the mobility of the anions at moderate temperatures, and without increasing the mobility of the cations.[2,3] It is crucial to develop methods for preparing novel solid state anion conductors and to gain fundamental understanding of the factors that influence the anion mobility in the materials. Hence the prepared materials will be characterized with different techniques and their properties and performance in (electro)chemical energy conversion and storage applications will be evaluated.

Currently, my efforts are mainly focused on chloride and hydroxyl ion conductors, with both polymer-based and inorganic materials being investigated. Some of the techniques I use are polymer film casting from solution and melt infiltration into porous scaffolds for synthesis, and powder XRD, IR spectroscopy, electrochemical impedance spectroscopy (EIS) and other electrochemical techniques for analysis. All experiments are performed under controlled/inert atmosphere.

[1] Z. Zhang *et al.*, *Energy Environ. Sci.* **11**, 1945-1976 (2018)
[2] C. Pfaffenhuber *et al.*, *Phys. Chem. Chem. Phys.* **15**, 18318 (2013)
[3] Z. Zou *et al.*, *Chem. Rev.* **120**, 9, 4169-4221 (2020)

Support effects in the gold-catalyzed direct propene epoxidation

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Sponsor: Since November 2017
Supervisors: prof. dr. Petra de Jongh, dr. Baira Donoeva

Gold nanoparticles, Selective oxidation, Catalytic testing

Supported gold nanoparticles (GNPs) have been studied in selective oxidations for several decades. Reactions that are catalyzed by GNPs include CO oxidation, 5-hydroxymethylfurfural oxidation and propene epoxidation. In 1998 Haruta et al. reported the application of GNPs supported on titanium based oxides in the vapor-phase oxidation of propene to propene oxide.[1] Nowadays many different systems based on GNPs and Ti-based materials (figure 1) are known for this reaction, however the best known catalysts based on Au supported on titanosilicate-1 (Au/TS-1) have shown limited conversion of propene to propene oxide and low reactant efficiency.[2] Notably, while it is known that the support is essential to the overall catalytic performance, the exact effect of the support is not well understood.

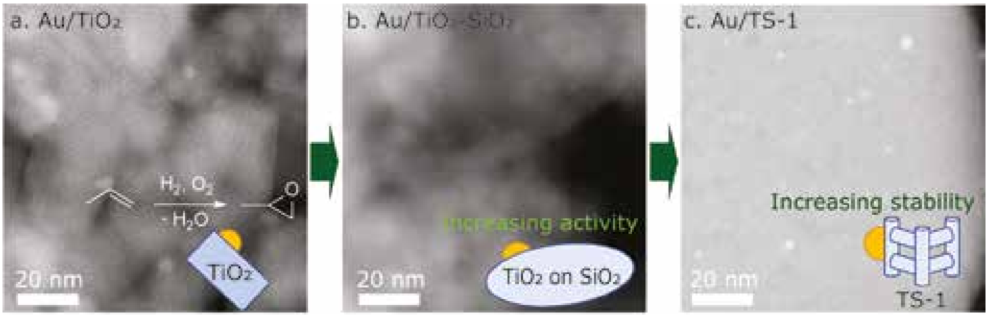

Figure 1: HAADF-STEM images of representative gold catalysts. a. Au/TiO_2, b. Au/TiO_2-SiO_2, c. Au/TS-1

With this project we investigate how support related parameters affect the selective oxidation of propene to propene oxide. We are particularly interested in modifications to enhance the catalyst's activity, stability and reactant efficiency in the selective oxidation of propene to propene oxide.
We demonstrate for example the role of Na-cations as promotor to enhance propene oxide selectivity.[3] In addition, we want to make a comparison between the catalytic behavior in terms of activity, stability and oxidant efficiency of modified catalysts in liquid phase epoxidations with H_2O_2 compared to the gas phase propene epoxidation.

The catalysts are characterized with XRD, DR UV-Vis, N_2 physisorption, TEM and HAADF-STEM. Their surface chemistry is studied in detail with IR with probe molecules, mass titrations. The performance of the catalysts is studied in the gas phase propene oxidation and liquid phase oxidations using H_2O_2 or O_2 as oxidant.

[1] M. Haruta, B.S. Uphade, S. Tsubota, A. Miamoto, *Res. Chem. Intermed.*, **24**, 329 (1998).
[2] A.K. Sinha, S. Seelan, S. Tsubota, M. Haruta, Angew. *Chem. Int. Ed.*, **125**, 16557 (2021).
[3] E.J.J. de Boed, J.W. de Rijk, P.E. de Jongh, B. Donoeva, *J. Phys. Chem. C*, **125**, 16557 (2021).

Preparation of bimetallic Pd-Ni/SiO2 nanoparticles for selective hydrogenation reactions

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Supervisors: prof. dr. Petra E. de Jongh, prof. dr. ir. Krijn de Jong and dr. Jessi van der Hoeven

Heterogeneous catalysis, Bimetallic nanoparticle synthesis, Electron microscopy

Bimetallic nanoparticles are interesting for use in heterogeneous catalysis as they offer modified properties compared to their monometallic constituents. Both Pd and Ni are highly active catalysts for hydrogenation reactions and it has been reported that bimetallic Pd-Ni nanoparticles demonstrate greater selectivity to certain products. Since the synthesis greatly impacts the Pd-Ni nanoparticles formed and consequently their catalytic performance, the goal of this research is to study the synthesis of these Pd-Ni nanoparticles to gain size, shape and composition control.

The main characterization technique is thereby electron microscopy. Using in-situ electron microscopy, the synthesized Pd-Ni nanoparticles can be studied under relevant conditions; i.e. the catalytic conditions intended.

Finally, liquid-phase hydrogenation reactions are used to probe the intimacy and efficiency in terms of activity, selectivity and stability of the produced Pd-Ni/SiO_2 catalysts.

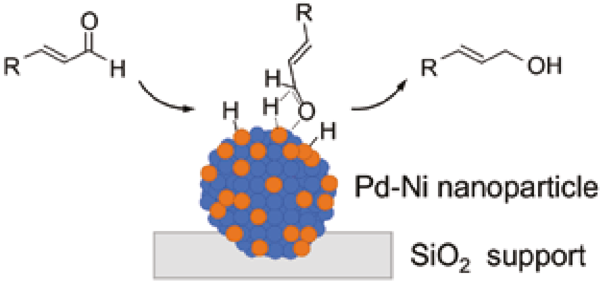

Figure 1: Schematic overview of a Pd-Ni/SiO_2 nanoparticle selectively hydrogenating an α,β-unsaturated aldehyde to an unsaturated alcohol.

[1] M. Luneau *et al., Chem. Rev.* **120**, 12834-12872 (2020)

Understanding solid-state electrochemical Interfaces from structure to function through first-principles calculations and machine learning

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Machine learning potentials, Solid-state Batteries, Electrochemical interfaces

Solid-state batteries are attracting worldwide interest as one of the modern technologies for safe batteries with high energy density. Substituting flammable liquid electrolytes used in conventional Li-ion batteries by solid electrolytes is considered a key strategy for improving safety and to facilitate the use of high-energy Li-metal anodes.[1] However, the design or discovery of solid electrolytes that provide not only sufficiently good ionic conductivity but are also compatible with energy-dense electrodes has remained a great challenge.

In actual solid-state batteries, solid electrolytes typically react with the electrodes at the interfacial layers and form a solid electrolyte interphase (SEI) at the negative electrode and a cathode electrolyte interface (CEI) at the positive electrode. The SEI and CEI can give rise to high resistance and low mechanical or electrochemical stability, leading to poor battery performance.[2] The atomic structures of the SEI and CEI are usually complex non-crystalline and evolve dynamically during charge-discharge cycling. A better understanding of the properties of the SEI/CEI and related phenomena, e.g., reduced Li-ion diffusion and electrochemical degradation, is crucial to the rational design of better solid-state batteries.

This research aims to improve the understanding of SEI structures and related properties at the atomic level, which determine the macroscopic properties of solid-state batteries. Machine learning potentials (MLP) will be trained on structure-energy relationships from a dataset of atomistic calculations based on density functional theory.[3-7] These MLPs will be used to construct realistic atomic-scale models of SEI structures and to study Li-ion dynamics and electrochemical reactions that occur at the interfaces during cycling using our machine-learning software package ænet (http://ann.atomistic.net).[3] The predictions from our model will be validated against experimental results that probed the SEI during the charge-discharge process performed by our experimental collaborators.

[1] R. Chen *et al. Chem. Rev*. **120**, 14, 6820–6877 (2020).
[2] Y. Xiao, G. Ceder, *et al. Nat. Rev. Mater*. **5**, 105–126 (2020)
[3] N. Artrith and A. Urban, *Comput. Mater. Sci.* **114**, 135-150 (2016).
[4] N. Artrith, J. *Phys. Energy* **1**, 032002 (2019).
[5] H. Guo, N. Artrith, *et al. Front. Energy Res*. **9**, 695902 (2021).
[6] T. Morawietz and N. Artrith *J. Comput. Aided Mol. Des*. **2**, 031001 (2021).
[7] N. Artrith *et al. Nat. Chem*. **13**, 505-508 (2021).

Cu-based catalysts for CO_2 hydrogenation to methanol

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CO_2 hydrogenation, Cu-base catalysts, Promoter effects

Methanol is one of the essential building blocks in the petrochemical industry but also can be considered as a potential fuel or energy carrier. Nowadays, methanol is industrially produced from synthesis gas over copper-zinc oxide catalysts supported on aluminium oxide.[1] Alternatively methanol can be produced by hydrogenation of CO_2.[2] In this sense the utilization of CO_2 can lead to a substantial reduction of greenhouse gas emissions.

Copper catalysts represent the main class of materials studied for the hydrogenation of CO_2 into methanol since copper is one of the few metals that does not adsorb CO dissociatively. To enhance the activity and the selectivity towards methanol formation, reducible oxides are added as promoters and/or support.[3] There is not yet a clear consensus on the nature of the active site and the mechanism by which promoters act.

The aim of this project is to explore particle size effects and metal-promoter interactions over copper-based catalysts for CO_2 hydrogenation to methanol. To achieve this, different synthesis techniques, such as controlled incipient wetness impregnation and deposition precipitation, will be employed to synthesize size-controlled metal nanoparticles supported on a well-defined and inert carbon support materials.[4] Long-term catalytic tests under industrially relevant conditions (high-pressure and high-temperature) will be employed to evaluated catalysts activity, selectivity and stability. Moreover, catalysts will be characterized by XRD, TEM(-EDX), TGA, TPR/D and synchrotron-based in situ X-ray absorption spectroscopy in order to gain novel insights into structure/activity relationship.

[1] K. C. Waugh, *Catal. Letters* **2012**, 142, 1153-1166.
[2] S. Dang *et al.*, *Catal. Today* **2019**, 330, 61-75.
[3] S. De *et al.*, *ACS Catal.* **2020**, 10, 23, 14147–85
[4] P. Munnik *et al.*, *Chem. Rev.* **2015**, 115, 6687-6718.

Metal hydride-based nanocomposites as solid electrolytes for all-solid-state batteries

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Electrochemistry, All-solid-state batteries, Metal hydrides

The development of energy storage technologies is crucial for the transition to a sustainable energy supply. Lithium-ion batteries are an effective means of energy storage, which is demonstrated by their wide application ranging from mobile phones to electric vehicles. Unfortunately, Li-ion batteries suffer from safety issues arising from their combustible electrolytes. All-solid-state batteries (ASSBs), in which the common liquid organic electrolyte is replaced by a solid electrolyte (SE), could potentially lead to safer batteries with increased energy density.

Recently, complex metal hydrides (e.g., $LiBH_4$) have gained attention as promising SEs due to their low density and high ionic conductivity at elevated temperatures. However, successful incorporation of metal hydride SEs in ASSBs requires sufficient ionic conductivity at room temperature. The goal of this project is to develop novel borohydride (BH_4^-)-based electrolytes with enhanced ionic conductivity at room temperature. Two strategies, partial ionic substitution[1] and interface engineering[2], as well as the combined approach are being explored (Figure 1a).[3,4] Interestingly, in interface engineered metal hydrides, a conductive interface layer forms between the metal hydride and the oxide (Figure 1b). This interface interaction is studied in further detail.

The SEs are studied with electrochemical impedance spectroscopy (EIS), XRD, IR, DSC and X-ray Raman scattering (XRS). Promising SEs are implemented in ASS Li batteries with different cathode materials. The electrochemical properties of the batteries and the nature and stability of the electrolyte/electrode interfaces are examined. This is achieved using electrochemical and synchrotron-based characterization techniques, including cyclic voltammetry, EIS and *operando* XRS.

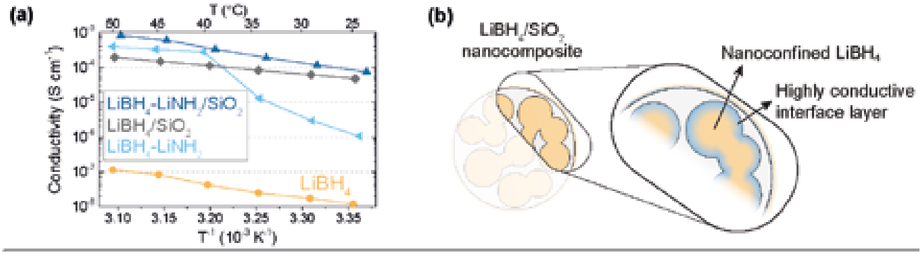

Figure 1: (a) Conductivity of $LiBH_4$ and $LiNH_2$-substituted $LiBH_4$ as well as their interface engineered counterparts[3] Schematic visualization of the metal hydride-metal oxide interface layer.

[1] H. Maekawa *et al.*, *J. Am. Chem. Soc.* **131.3**, 894-895 (2009)

[2] D. Blanchard *et al.*, *Adv. Funct. Mater.* **25.2**, 184-192 (2015)

[3] R. Zettl *et al. J. Phys. Chem. C*, **124.5**, 2806-2816 (2020)

[4] L. M. de Kort *et al. J. Mater. Chem.* **8.39**, 20687-20697 (2020)

Metal (oxide) – solid acid bifunctional catalysts for hydroconversion of n-alkanes

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Bifunctional catalysts, Hydroconversion of n-alkanes, Zeolites

Bifunctional catalysts play a significant role in modern petroleum refining.[1] In these catalysts a metal (oxide) function and a solid acid site are combined for the conversion of carbonaceous feedstocks into clean diesel and jet fuel. Ideally, renewable feedstocks, such as Fischer-Tropsch wax [2] or algae based hydrocarbons [3], are used to produce these fuels.

The metal site – which is typically Pt or Pd - performs dehydrogenation of alkanes into alkenes. The solid acid – typically a zeolite – catalyzes isomerization and cracking of these alkenes. The resulting alkenes then diffuse to the metal sites to get hydrogenated again. Previously, it has been shown for Pt/alumina/zeolite-Y catalysts that the distance between the active sites plays a key role in catalyst selectivity.[4] When the Pt nanoparticles are inside the zeolite crystals, both hydroisomerization and hydrocracking occur (figure 1a). Locating Pt nanoparticles on the binder results in an increased selectivity towards hydroisomerization because of improved mass transport of reactants and intermediates from the acid site to the metal site and *vice versa* (figure 1b).

In this project we aim to extend the understanding of selective conversion of n-alkanes by these bifunctional catalysts using alternative solid acid functions and (non-noble) metal (oxide) particles. Furthermore, the effect of lower Pt and Pd loadings is studied. The catalysts are characterized using techniques such as HAADF STEM, XPS, Pyridine-FT IR and catalytic tests are performed using a 16-parallel reactor system (Flowrence, by Avantium).

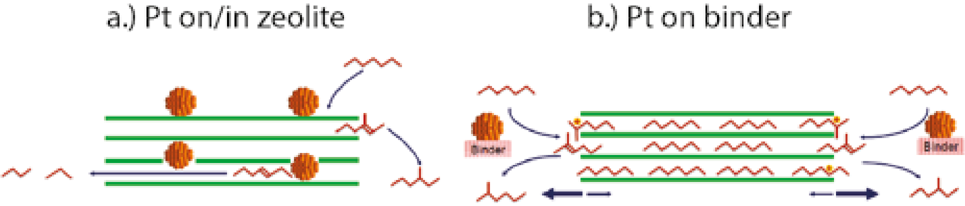

Figure 1: Schematic representation of hydroconversion of n-heptane over a Pt/zeolite/binder bifunctional catalyst with a.) Pt nanoparticles on/in a zeolite crystal, and b.) Pt nanoparticles on a binder material (typically ${}_{\gamma}$-Al_2O_3).

[1] J. Weitkamp, *ChemCatChem* **4**, 292-306 (2012)
[2] C. Bouchy *et al., Oil Gas Sci. Technol.* **64**, 91-112 (2009)
[3] N.H. Tran *et al., Fuel* **89**, 265-274 (2010)
[4] J. Zečević *et al., Nature* **528**, 245-248 (2015)

New electrodes for CO_2 conversion: nanomorphology and composition

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Sponsor:	RELEASE consortium
Supervisors:	prof. dr. P.E. de Jongh, dr. P. Ngene

Electrocatalysis, Porous metals, Bimetallic catalysts

Electrochemical CO_2 reduction is promising to overcome the intermittent nature of renewable energy sources and close the carbon cycle. Different metals have been investigated as catalyst for the electrochemical CO_2 reduction reaction and they can be divided in to three groups based on the products they make: 1) CO producing metals (such as Ag, Au and Zn); 2) COOH producing metals (such as In, Sn and Pb); and 3) H_2 producing metals (such as Fe, Ni, Pt, Pd). Cu behaves different, as it is the only metal that is capable of producing C_{2+} products.[1,2,3] It is known that these product specificities are related to the binding strength with the different reaction intermediates.[1] However, the performance of the catalysts is not well enough understood to tune the product formation based on rationally designed catalysts. Hence, more research is needed to fundamentally understand the performance of the electrode and relate its composition and morphology to the catalytic activity, selectivity and stability.

In order to obtain a better understanding, in my project two types of catalysts are studied in more detail, namely bimetallic catalysts and nanoporous metals. Bimetallic catalysts could have an optimized binding to the reaction intermediates due to both geometric and electronic effects. When bimetallic catalysts are considered, both the composition (which metals and which ratio) and the morphology (e.g. mixed phase, core-shell particle or layered phase) can affect the performance.[2] Nanoporous metals are interesting to investigate, as they have a high surface area and more low-coordinated sites.[3] Nanoporous metals can for example be prepared via dealloying or by use of a sacrificial template.

[1] Bagger *et al.*, *ChemPhysChem*, **18**, 3266–3273 (2017)
[2] He *et al.*, *ChemSusChem*, **11**, 48–57 (2018)
[3] Lu *et al.*, *Nano Energy*, **29**, 439–456 (2016)

Femtosecond XAS and RIXS of transition metal oxides

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Sponsor: MSCA-ITN and UU, since April 2021

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X-ray spectroscopy, X-ray free-electron laser (XFEL), High harmonic generation (HHG)

The advancement of photoanode materials with apt properties plays a pivotal role in photoelectrochemical (PEC) water splitting. As promising candidates, perovskites appertain to a class of compounds with the prevailing formula of ABX_3, where the A site is inhabited by the larger cation (e.g., La^{3+}, Ca^{2+}, Ba^{2+}, Sr^{2+}), while the B by the smaller cation (e.g., Ti^{4+}, Fe^{3+}, Co^{3+}); X is generally oxygen.[1]

The emergence of X-ray free-electron lasers (XFELs), which delve into the atoms and molecules on femtosecond (fs) time scales (10^{-15} s), is an important stepping stone to unprecedented discoveries. Moreover, the development of table-top extreme ultraviolet (XUV)/soft X-ray laser sources with attosecond (10^{-18} s) pulse employing high-order harmonic generation (HHG) has paved the way to study ultrafast dynamics currently out of reach at the XFELs.[2]

Our group has recently reported the first investigation of the ultrafast charge carrier dynamics in copper tungstate ($CuWO_4$) employing time-resolved optical and X-ray spectroscopies[3], in which, an elevated charge density at the Cu site with a decay time of 400 fs has been unveiled by tracking a 50 fs, 3.1 eV optical laser excitation in $CuWO_4$ via a pump-probe delayed X-ray excitation 1.0 eV before the Cu L_3 edge (Fig. 1).

In this project, we will prepare $LaBO_3$ (B = transition metal) perovskite samples by the pulsed laser deposition (PLD) technique at Twente University, which will be followed by their preliminary characterization using AFM, STEM, XRD, and XPS techniques. Then, to shed light on the electronic structure of these materials, we intend to utilize both table-top fs soft X-ray sources at the Max Born Institute (MBI) for Nonlinear Optics and Short Pulse Spectroscopy in Germany for 3p XAS and compare the results with fs 2p XAS performed at XFELs, e.g., PAL-XFEL, and static 2p3d RIXS performed at synchrotrons. In addition, we will perform multiplet calculations to interpret the fs-XAS and fs-RIXS experiments. In particular, we will further develop the 3p XAS and RIXS calculations.

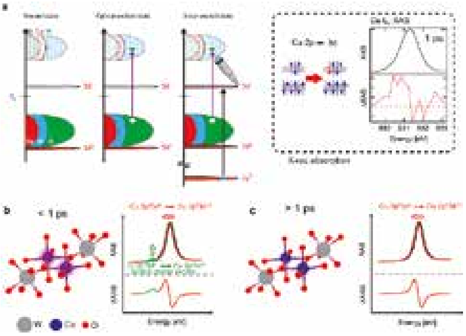

Figure: 1 (a) The optical and X-ray excitation processes in $CuWO_4$ and the Cu L_3-edge transient XAS spectra at a delay time of 10 ps. Illustrations of the charge density at Cu sites in $CuWO_4$ after photoexcitation below a delay of 1 ps (b) and above a delay of 1 ps (b) and above a delay of 1 ps (c).

[1] Dias, J. A. *et al.*, *ChemElectroChem* **7**, 3173–3192 (2020).
[2].Vura-Weis, J. *et al.*, *J. Phys. Chem. Lett.* **4**, 3667–3671 (2013).
[3]Uemura, Y. *et al.*, *J. Phys. Chem. C* **125**, 7329–7336 (2021).

Understanding the degradation and increasing the lifetime of electrodes and membranes under harsh operating conditions

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Electrocatalysis, Stability, In-situ characterization

The electrochemical conversion of CO_2 into value-added products using renewable electricity is a promising solution for both the rising levels of CO_2 in the atmosphere and the mitigation of electrical peak loads associated with intermittent renewable energy sources. The electrochemical CO_2 reduction reaction can be catalyzed by several different transition metals, each yielding different reaction products. Thus far, Cu is the only transition metal shown to facilitate C-C coupling and form C_{2+} products like hydrocarbons and alcohols in significant amounts. However, a wide range of products is formed. Therefore, much research has focused on improving the selectivity of Cu-based cathodes, as well as reducing the overpotential required to drive this reaction.[1]

A different problem is the stability of the electrodes, as their structure and hence their performance are strongly affected by the application of an electrical potential.[2] This effect is more pronounced at higher current densities, which are required for industrial applications. Therefore, it is important to increase understanding on the degradation mechanisms of electrodes. This requires more knowledge on the changes in the electrocatalyst morphology over time. Ex-situ characterization techniques are insufficient, because they do not image the electrodes under relevant reaction conditions.

Therefore, the aim of this project, which is part of the RELEASE consortium, is to understand more about the degradation mechanisms of Cu-based electrodes for the CO_2 reduction reaction under harsh operating conditions. This will be done using conventional structural and electrochemical characterization techniques, as well as advanced *in-situ* characterization techniques like XAS and TEM.[3,4]

[1] S. Nitopi *et al., Chem. Rev.* **119**, 7610-7672 (2019)
[2] K. Han *et al., ChemCatChem* **13**, 1998-2004 (2021)
[3] J. Timoshenko *et al., Chem. Rev.* **121**, 882-961 (2021)
[4] R.M. Aran-Ais *et al., Nat. Commun.* **11**, 1-8 (2020)

TEM and HR-TEM ex situ and in situ studies of supported catalysts

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In situ S/TEM, High resolution S/TEM, Supported catalysts

Transmission electron microscopy (TEM) has the necessary resolution and flexibility to characterize catalysts at magnifications spanning five orders of magnitude, from micrometer- to atomic-level, via imaging, electron diffraction and spectroscopy. It can provide detailed structural information of catalysts, e.g., particle size distributions, shape of metal NPs, composition of NP surfaces, surface structure, crystal structure. With the analytical accessories of energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS), chemical information can be examined at the atomic scale. Combined with in situ techniques, it even enables scientists to characterize the structure changes of the catalysts during reaction in gas[1] or liquid phase. My research focuses on using high resolution TEM (HR-TEM) and in situ TEM to study supported catalysts at atomic- and nanometer- scale.

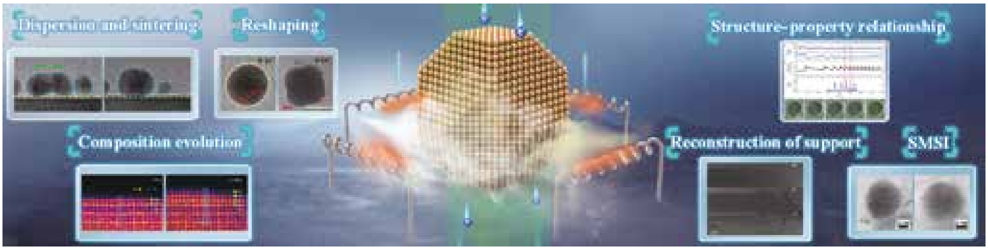

Figure 1: The structural evolutions of catalysts by using *in situ* gas S/TEM.

[1] M. Tang *et al.*, *ACS Catal*. **10**, 14419-14450 (2020)

Particle size, support and promoter effects of carbon supported nickel catalysts for CO_2 hydrogenation

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CO_2 hydrogenation, Supported nickel nanoparticles, *In situ* transmission electron microscopy

CO_2 methanation is a valuable reaction to decrease CO_2 emissions and store renewable energy in synthetic natural gas. Nickel is widely investigated as catalyst for this process due to its high hydrogenation activity and natural abundance. The mechanism of CO_2 methanation depends on many factors, such as the type of support used and the metal particle size. As a result, it a challenging reaction to understand in full detail.

In this project I focus on the synthesis of carbon supported nickel catalysts with various nanoparticle sizes. A carbon support changes the metal support interaction compared to oxidic supports and can limit the formation of spectator species, especially with the addition of extra metal oxides that enhance the catalytic performance (promoters). Good control over the catalyst preparation, including nanoparticle deposition and distribution, allows the study of metal particle size effects on the catalytic stability, activity and selectivity. The catalyst performance is evaluated in long-term, high pressure CO_2 hydrogenation to methane, mimicking industrial Power-to-Gas conditions. The incorporation of several types of functional groups on the support surface, both acidic and basic, is used as a tool to improve the catalyst stability and studied in detail.

Advanced characterization techniques such as H_2-TPR, TGA-MS, XRD, TEM provide knowledge about a catalyst before and after the reaction. However, the ultimate goal is to study the catalyst behavior under reaction conditions. A special focus in my research is on the use of gas-phase transmission electron microscopy. This recently developed technique allows the unique opportunity to visualize catalysts at nanometer scale while being exposed to reaction gasses at atmospheric pressure and elevated temperatures.[1] With this approach I aim to better understand the catalyst dynamics under operational conditions, focusing on nanoparticle restructuring and movement in gas atmosphere in the absence and presence of promoters.

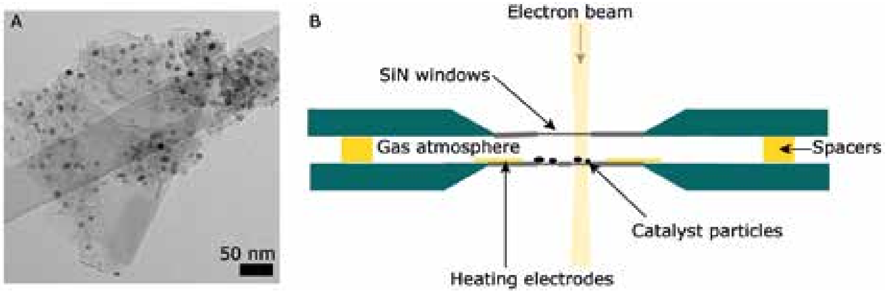
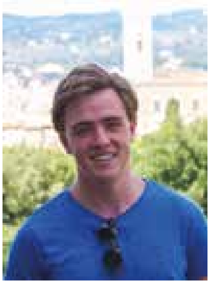


Figure 1: a) TEM image of carbon supported nickel nanoparticles and b) schematic representation the gas cell used for *in-situ* gas phase TEM studies.

[1] L.I. van der Wal *et al.*, *Catal. Sci. Technol.*, **11**, 3634-3658 (2021)

Selective hydrogenation of polyolefins



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Sponsor: since October 2019
Supervisors: prof. dr. P.E. de Jongh, dr. J.E.S. van der Hoeven
Selective hydrogenation, Heterogeneous catalysis

Selective hydrogenation of poly-unsaturated hydrocarbons is a challenging process with great relevance for a wide range of industrial applications, such as the purification of high purity polymer-grade olefins. In such processes, polyolefin impurities (e.g. butadiene or acetylene) are removed from alkene gas streams (e.g. propene or ethylene). These impurities are detrimental for product quality and cause severe deactivation of polymerization catalysts.

As a model reaction we are investigating the semihydrogenation of 1,3-butadiene to butenes in a propene-rich gas-stream. Traditionally supported noble metals, such as palladium, have proven to be very efficient hydrogenation catalysts. However, with high activity, selectivity is often poor and overhydrogenation to butane and propane may occur, especially when operating near full butadiene conversion. For this process the optimal catalyst retains a high selectivity to the alkene product, even close to full conversion of the poly-unsaturated hydrocarbon.

In this project we focus on the preparation, characterisation and catalytic testing of supported (noble) metal catalysts for the selective hydrogenation of small poly-unsaturated organic molecules. This includes rational synthesis design of supported catalysts, from single atoms to large nanoparticles. Fundamental studies into the genesis of the catalyst is being performed with advanced characterisation methods such as STEM-EDX and EXAFS. The catalytic structure-performance relationship will be studied by monitoring selectivity, activity and stability under industrially relevant reaction conditions.

Syngas reaction with light olefins to produce high value products

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Single atom catalysts, Sustainability, Hydroformylation

The oxo process, discovered by Otto Roelen in 1938, represents one of the most atom economic, straightforward approaches to the preparation of aldehydes starting from olefins and syngas in the presence of a metal catalyst. This reaction is still nowadays the most applied catalytic process in industry to produce more than 6 million tons every year of aldehydes widely used for the synthesis of pharmaceuticals, polymers, food, fragrance and agrochemicals compounds.[1]

Currently, phosphine-ligand-containing Rh complexes are mostly applied in industrial processes because of their superior catalytic activity. However, the catalyst separation issue remains unsolved.

Heterogeneous catalysts (especially ligand-free ones) are more suitable for industrial applications owing to the convenience of recovering and recycling. Consequently, tremendous efforts have been dedicated for the heterogenization of homogeneous catalysts but with limited success.

Designing new catalysts that combine the advantages of both hetero- and homogeneous ones throughout non-conventional pathways will be the main challenge.

[1] L. Wang *et al.*, *Nat. Commun.*, **7**, 14036-14043 (2016).

Operando x-ray spectroscopy of the oxygen evolution reaction

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Sponsor: CSC, since December 2020
Supervisors: prof. dr. Frank de Groot, dr. Petra de Jongh

X-ray spectroscopy, Operando, Oxygen evolution reaction

Operando x-ray spectroscopy is one of most powerful techniques to investigate the catalytic mechanism and the accurate identification of active sites in (electrochemical) heterogeneous catalysis.[1,2] 3d transition metal (hydro)oxides like La(Sr)TMO$_3$ (TM = Fe, Co, Ni and Mn), are actively investigated in relation to replace 5d based systems (e.g., Pt). The interface is critical for high performance due to its highly disordered structure differing from the bulk phase. In this project, we plan to conduct experiments for OER and ORR using operando X-ray spectroscopy. We combine (near) atomic spatial resolution to characterize catalysts under different levels conditions.

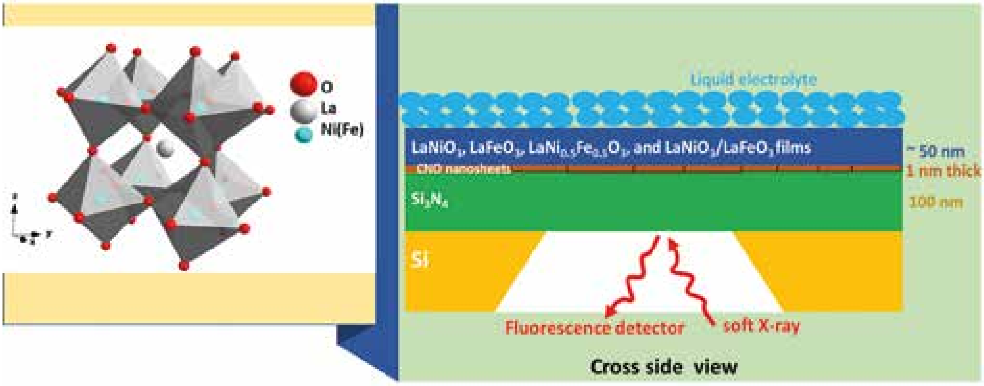

Figure 1: The diagram of perovskite structure and operando XAS for OER catalysis.

[1] J. Timoshenko *et al.*, *Chem. Rev.* **121**, 882–961 (2021).

[2] F. de Groot *et al.*, *J. Electron Spectrosc. Relat. Phenom.* **249**, 147061 (2021).

Studying the synthesis of nickel catalysts using in situ gas and liquid phase TEM

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***In Situ* gas phase TEM, *In Situ* liquid phase TEM, Catalyst synthesis,**

Supported metal catalysts are vital to the chemical industry and are likely to be the foundation for sustainable energy solutions in the future. The procedure used for the synthesis of the catalyst determines the size, shape, and dispersion of the active metal nanoparticles across the support material and therefore the activity, stability and selectivity of the final catalyst.

Catalyst synthesis is mostly optimised by trial and error: make many catalysts by varying the procedure and see which one works the best. This method of optimising catalyst synthesis procedure is effective but not efficient. A smarter approach would be to design the perfect combination of synthesis steps to make the perfect catalyst on the first attempt. This goal requires that we understand exactly what is happening in every step of the synthesis and what effect it has on the final catalyst's properties.

Developing this understanding is challenging for a few reasons:

1. Catalysts consist of nanoparticles which must be visualised using an expensive specialised piece of equipment called a transmission electron microscope (TEM).
2. Catalysts are synthesised in multiple steps taking place in liquids or gasses at high temperatures and pressures.
3. TEM only work under ultra-high vacuum conditions, otherwise they break.

New gas and liquid cell technology enables the introduction of gas or liquid environments in small sealed regions around the sample to protect the microscope (Figure 1 a.). My research uses this technology to perform catalyst synthesis in situ inside the TEM. We hope that the ability to visualise the processes occurring during catalyst synthesis will improve our understanding of the reactions at play and put an end to trial and error synthesis. I focus on nickel catalysts as a model system and study deposition precipitation, drying and reduction (Figure 1.b).

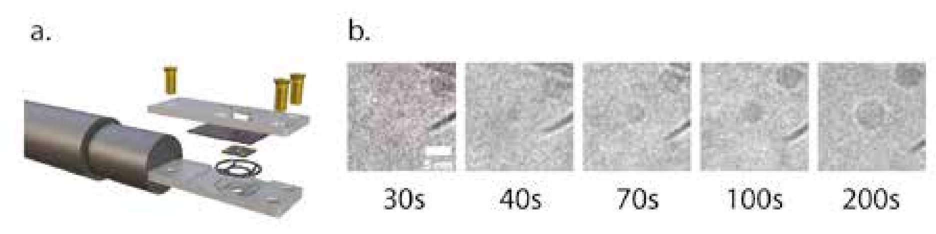

Figure 1: a. Depiction of the gas or liquid cell holder design wherein two silicon nitride chips encase the sample and are sealed using a gasket, b. example of in situ reduction where a 5 nm nickel particle grows from a nickel phyllosilicate precursor at 500°C under 1 bar of 5% H_2/Ar over the course of 200 seconds.

Design of Ni-based catalysts to study the carbon nanofiber growth during the thermal catalytic decomposition of methane

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Sponsor: Industry/ARC-CBBC, since October 2019
Supervisors: prof. dr. Petra de Jongh, prof. dr. ir. Krijn de Jong

Carbon nanofibers, Methane, Nickel catalysts

Over the past decades, extensive research has been done regarding renewable energy. Thermal catalytic decomposition of methane gas is one of the reactions that has gained a lot of attention. During this reaction, pure hydrogen is produced without the emission of CO_2. In addition, valuable carbon nanomaterials, such as nanofibers (CNF), single or multiwalled carbon nanotubes (CNT), are grown. These carbon nanomaterials have interesting properties, e.g. high electron conductivity, mechanical and thermal stability.[1][2]

The most commonly used catalysts are transition metals such as, Ni, Fe and Co supported on different inert materials.[1][2] Methane molecules adsorb on the metal surface, where the C-H bonds are broken. H_2 is formed and the carbon is transported through the particle or over the surface. Thereafter, it is deposited in graphitic layers forming CNTs or CNFs. The growth is influenced by many parameters, and therefore, the exact mechanism is not yet fully understood. An example of a proposed mechanism is shown in figure 1.

Nickel catalysts are known to provide high activity and are the most studied catalysts for this reaction. As the reaction has an endothermic nature, the conversion will increase when using higher temperatures. Unfortunately, Ni catalysts deactivate quickly at temperatures > 600 °C, as the surface is encapsulated by carbon. Using bimetallic catalysts can improve the catalyst in terms of activity and life time. It was found that addition of copper results in longer life times as the diffusion rate of carbon is increased, thereby keeping the surface available for the adsorption of methane.

In my research, I design Ni-based catalysts to study the influence of catalyst composition and morphology on the carbon yield and structure. I would like to understand the growth of the carbon nanostructures in order to tune structure of the end-product.

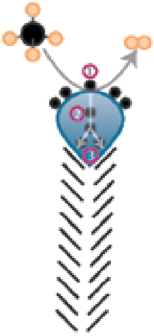

Figure 1: Schematic representation of the decomposition of methane. 1) Decomposition of methane at the surface. 2) Transport of carbon through the metal. 3) Deposition carbon in graphitic layers. Adapted from [1]

[1] K. de Jong *et al.*, *Catal. Rev. Sci Eng. CATAL. REV.*, **4**, 481-510 (2007)
[2] Muhammad *et al.*, *Int. J. Hydrog. Energy*, **41**, 18713-18734 (2018)

Gas-cell electron microscopy studies on methane decomposition into solid carbon and hydrogen gas using Ni-based catalysts

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Supervisors: Prof. dr. Petra de Jongh, prof. dr. ir. Krijn de Jong

In-situ electron microscopy, Carbon nanofibers, Methane decomposition

We study the decomposition of methane into hydrogen while growing carbon materials using Ni-based catalysts. Methane is a readily-available, cheap feedstock, but due to CO_2 emissions it is not ideal for use as fuel. Decomposition of methane into the clean fuel hydrogen while creating solid carbon is a promising alternative. Transmission electron microscopy (TEM) will be the main technique to study this process as it allows us to look at nanomaterials at nanometer spatial resolution. In previous work an environmental TEM was employed to study nanofiber growth at millibar pressures.[1] Using gas-cell in-situ TEM we intend to study the nucleation and growth phase of carbon filaments from methane in more relevant conditions, by varying parameters such as temperature, feed composition, pressure, but also catalyst size, composition and shape. Unique information from in-situ TEM experiments about carbon filaments growth and entanglement on a single particle level will be linked to process conditions and catalyst structure. The in-situ TEM experiments will be critically compared to results in more conventional experiments.

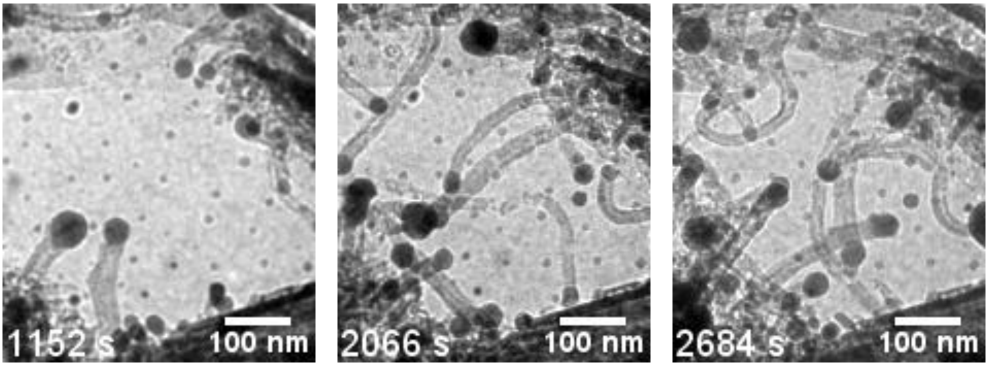
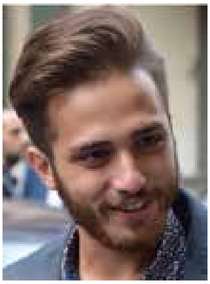


Figure 1: In-situ TEM images of the growth of carbon nanofibers on Nickel-Copper particles (3:1 Ni:Cu ratio) on a carbon support at atmospheric pressure with 10% hydrogen, 30% methane and 60% argon gas.

[1] S. Helveg *et al.*, *Nature* **427**, 426-429 (2004)

New generations solid-state batteries



Valerio Gulino, v.gulino@uu.nl

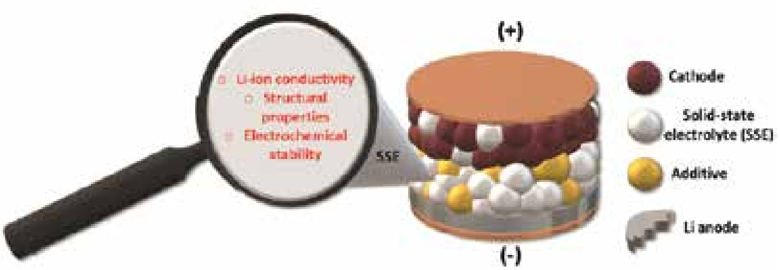
Sponsor: NWO Echo grant, since November 2020

Supervisors: prof. dr. Petra de Jongh, dr. Peter Ngene

Solid-state electrolyte, Li-ion battery, Complex hydride

Nowadays, battery electrolytes typically consist of lithium salts dissolved in flammable organic solvents. Improved solid electrolytes (SEs) would facilitate the development of several emerging technologies, such as high capacity all solid-state batteries. In fact, owing to a very low reduction potential, Li metal is the most desirable anode for high-power applications, but its use in conventional batteries is hampered by the uneven Li plating that results in dangerous shortcuts. SEs could prevent dendrite growth, hence overcoming the risks associated with flammable organic solvents and increasing the lifetime of the device.[1] Various types of solid-state ionic compounds, including complex hydride, have been shown their capacity to conduct ions.[2] An essential requirement for a solid-state ion conductor to be used as an electrolyte in a battery is a high ionic conductivity at RT (higher than 10^{-3} S cm^{-1}).[3] Different approaches have been used to increase the conductivity at RT. Substitution of the anion by halides or complex anions can either stabilise high temperature structure or promote the formation of new compounds with improved ionic conductivity at RT. A different approach to increase the ionic conductivity is by mixing the ionic conductor with oxides to form a composite, e.g. by nanoconfinement in suitable scaffolds or by ball milling.

The aim of the project is developed novel hydride-based solid-state electrolytes using both anion substitution and interface engineering approaches. The synthesis will be performed by ball milling or by Nanoconfinement. Subsequently, the electrochemical proprieties (e.g. the electrochemical stability and ionic conductivity) of novel fast ion conductors will be studied using several electrochemical characterization techniques (e.g. Cyclic voltammetry and Electrochemical Impedance Spectroscopy). Finally, the electrolyte will be implemented in different all-solid-state Li batteries. Different cathode materials could be used to optimize the battery performance.



[1] J. B. Goodenough *et al.*, *J. Electrochem. Soc.* **162**, A2387–A2392 (2015)

[2] M. Matsuo *et al.*, *Adv. Energy Mater.* **1** (2), 161–172 (2011)

[3] J. C. Bachman *et al.*, *Chem. Rev.* **116** (1), 140–162 (2016)

Bifunctional catalysts convert syngas to Methonal and DME

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Supervisors: prof. dr. Petra de Jongh

Syngas conversion, Structure-performance relationship, Electron microscopy

DME can be used as an excellent alternative to diesel fuel due to its high cetane number (55–60) and a low emission of CO, NO_x in the exhaust gases from a diesel engine as it has no C-C bond structures.

Two main chemical transformation routes were reported in the literatures for the conversion of syngas into fuels, Fischer-Tropsch route and syngas to methanol which gives dimethyl ether (DME) by dehydration. The direct DME synthesis, which simultaneously triggers methanol synthesis and in-situ dehydration, is integrated in bifunctional catalysts in a single reactor. And how the two catalytic functions can work in a complete "synergistic effect" through being finely dispersed by maintaining a close proximity but not reacting each other is still a big challenge. Explore the structure-performance relationship between activity selectivity and stability by adjusting the proximity of the two components and modifying the support.

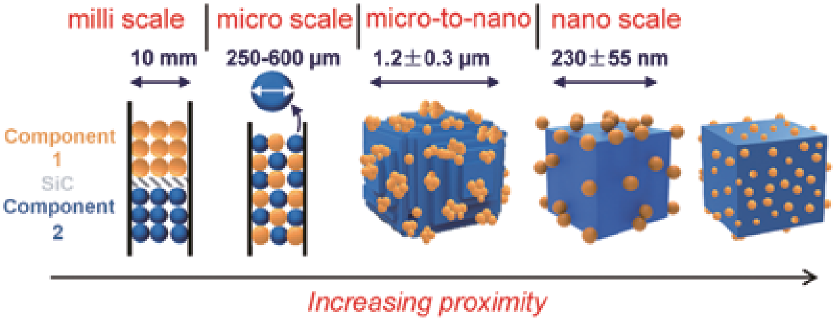
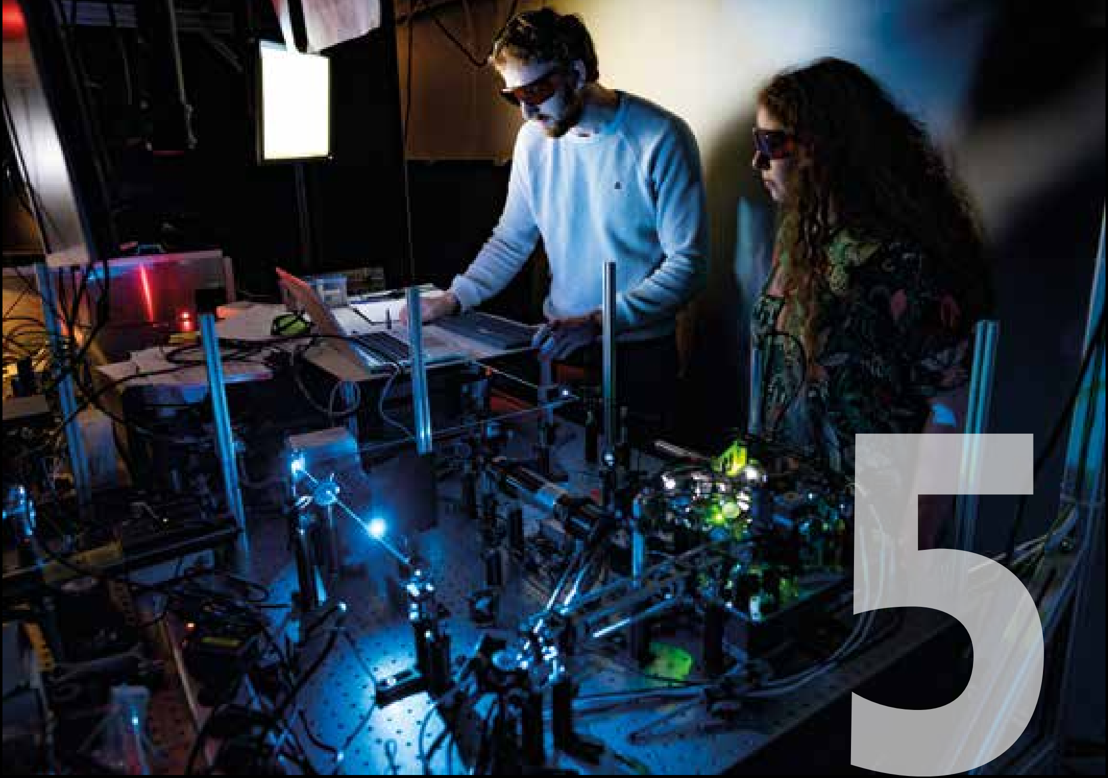


Figure 1: Different proximity of two component, modified from references [3]

[1] N. Tsubaki *et al.*, *Appl. Catal. B: Environ.*, **217**, 494–522 (2017)

[2] A. Corma *et al.*,*Adv. Mater.*, **2002927** (2020)

[3] Y. Wang *et al.*, *Chem. Sci.*, **9**, 4708 (2018)



5

NANOPHOTONICS

Scientific staff	prof. dr. Peter van der Straten, prof. dr. Allard Mosk, dr.ir. Sanli Faez, dr. Dries van Oosten
Technical support	Aron Opheij, Paul Jurrius, Dante Killian
Administrative staff	Mijke Heldens
PhD students/Postdocs	10

Research Mission

The Nanophotonics group aims to control light, matter and their interactions at the nanoscale. Light-matter interactions allow us to create and study extreme states of matter, ranging from quantum phenomena in space-time crystals made of ultracold atoms, to superheated plasmas in laser ablation. We develop and use methods to shape and measure the wavefront of light, and use these in imaging, focusing and precise optical measurements as well as novel schemes for energy-efficient optical information processing. Precise optical measurements of nanoscale surface scattering allow us to detect processes of interest to biomedical applications as well as study basic processes in energy storage materials.

Electrophoretic tracking of single extracellular vesicles

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Sponsor: NWO, since February 2021
Supervisors: dr. ir. Sanli Faez

Single-particle tracking, Scattering, microscopy, biosensing

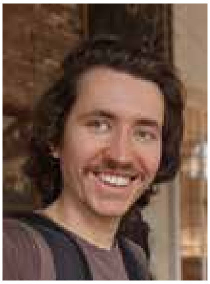
Cells release extracellular vesicles (EVs), which are heterogeneous particles showing inherently similar intrinsic properties as their parent cell, such as mRNA, DNA, proteins and receptors. Those vesicles serve for the intercellular communication, coagulation, and waste and drug management in our bodies. Changes in their concentration and protein content may act as potential biomarker for various diseases. For this purpose, we need to accurately visualize and characterize EVs. However, the particles in this range are not easily detectable with common optical methods. One challenge is their broad distribution in size, ranging from 30 nm to 1 µm. For the smallest particle, their low refractive index makes them weak scatterers and therefore hard to track.
The goal is to build a sensitive optical detection platform, which simultaneously enables tracking single EV's to characterize their size, concentration, fluorescent labels, dynamics, and mutual interactions. Additionally, the system should reliably detect the smallest EV's at high throughput (>1 kHz). That requires a high signal-to-noise ratio and a dark and stable background. Our method of choice is based on Rayleigh scattering and characterizing the electrochemical properties of single EVs.

The nanometric particles are visualized and manipulated by operating with a home-built total internal reflection microscope, later extending it with fluorescence. The sample is prepared by creating a microfluidic channel in between two microscope slides, where nanoparticles are suspended in DI water. By illumination at the total internal reflection, we also create a high sensitivity to the distance of the particle from the interface (see Figure 1). One of the main challenges of scattering microscope is separating the scattering from particles from that of the background speckle, which is the reason for building a customized setup.

The methods developed in this research will be applied to the envisioned applications in medical diagnostics in collaboration with our consortium partners at the Amsterdam UMC and Dispertech BV.

Figure 1: Schematic of experimental set-up.

Lensless imaging using an optimization framework based on automatic differentiation



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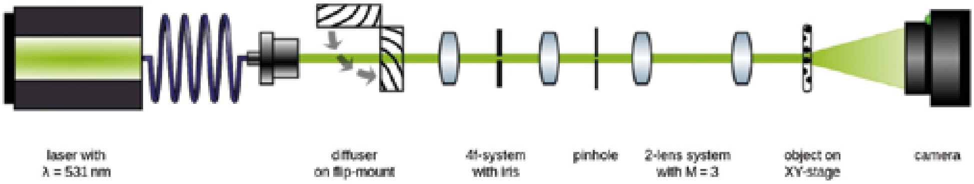
Sponsor: NWO, ASML, since December 2018
Supervisors: prof. dr. Allard P. Mosk, dr. Dries van Oosten

Coherent diffraction imaging, computational imaging, machine learning

Ptychography is a computational imaging method that allows for wavefront sensing and phase-sensitive microscopy from a set of diffraction patterns. Recently, it has been shown that the optimization task in ptychography can be achieved via automatic differentiation (AD). In our project, we develop an AD-based framework implemented with TensorFlow, a popular machine learning library. This enables us to solve the reconstruction problem in ptychography using a layer-by-layer approach, akin to the architecture of deep neural networks. As a result, our framework is highly modular, and it is straightforward to extend the physics model or implement specific cost functions, which is not always possible using conventional methods. Lastly, the layered architecture makes our AD-based framework interesting for the emergent idea of interfacing a deep neural network directly to the forward model ("cascaded neuronal network").

Our experimental setup is shown in the figure below. Some features worth mentioning are: resolution in the order of 1 µm, quantitative phase and amplitude retrieval, wavefront retrieval, free of aberrations, "infinitely" large field of view (limited only by the range of our scanning stage and memory), multi-mode reconstruction, GPU-accelerated.



High resolution mode mapping in a nonlinear photonic crystal nanocavity

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Sponsor: NWO-Vici, since Aug. 2017
Supervisors: prof. dr. Allard Mosk, dr. Sanli Faez
Photonic Crystal Nanocavities, Optical Nonlinearity, Optical telecommunication and computing

Photonic crystals are periodic dielectric structures that prohibit the propagation of light in the bandgap in certain directions. They hold the ability to control the flow of light and are therefore of great interest in telecommunication and the development of photonic integrated circuits. Two-dimensional photonic crystal membranes – e.g. a pattern of airholes in a thin slab of semiconductor material – can be designed to contain waveguides and nanocavities. These 2D photonic crystals have shown interesting phenomena, such as all-optical switches, optical memory, and reconfigurable circuits. The optical nonlinearities in these crystals play a key role in developing systems where light is a data carrier. Additionally, knowledge about the optical mode profile is crucial of all of these functions.

In this project we demonstrate the possibilities of an InGaP photonic crystal membrane with mode-gap cavities on the waveguide [1-4], specifically in the optical nonlinear regime. A schematic of the membrane is shown in Fig. 1a. Infrared light is coupled in from the side and probes high-Q resonators on the waveguide. The modes in the resonators can be excited with an optical out-of-plane pump beam that scans the surface and locally heats the membrane. Since thermo-optical nonlinearity is known to be present in the material [5], the pump will cause a redshift of the resonance (see Fig. 1b). This thermo-optical effect can be optimized by combining the optical pump with a high-power probe. The free carriers created by the pump will then absorb probe light and contribute additional heat in those places where the pump spot overlaps with the mode profile. Using this method we image the same mode profile at high probe power and achieve subwavelength resolution, observing details in the mode profile we could not measure in the linear regime (see Fig. 1c).

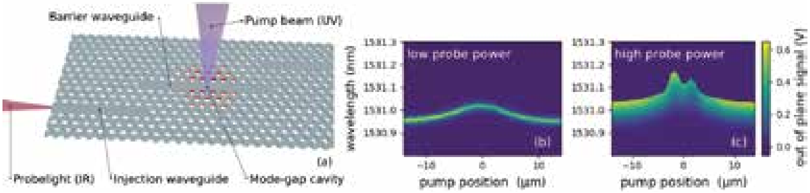


Figure 1: (a) Schematic of the photonic crystal membrane holding a mode-gap cavity on the barrier waveguide. (b) Cross section of the optical mode profile of mode-gap resonance at low probe power (linear regime). (c) High-resolution cross section of the optical mode profile at high probe power (nonlinear regime), this time revealing the double peak of the first higher order mode of the cavity that remained undetected in the linear regime.

[1] E. Yüce, J. Lian, S. Sokolov, J. Bertolotti, S. Combrié, G. Lehoucq, A. De Rossi, A. P. Mosk, *ACS Photonics* **5**, 3984-3988 (2018)

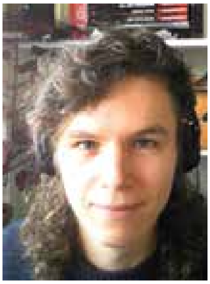
[2] S. Sokolov, J. Lian, S. Combrié, A. De Rossie, A. P. Mosk, *Appl. Opt.*, **56**, 3219-3222 (2017)

[3] J. Lian, S. Sokolov, E. Yüce, S. Combrié, A. De Rossi, A. P. Mosk, *Opt. Express* **24**(19), 21939 (2016)

[4] S. Sokolov, J. Lian, E. Yüce, S. Combrié, G. Lehoucq, A. De Rossi, A. P. Mosk, *Appl. Phys. Lett.* **106**, 171113 (2015)

[5] K. Perrier, S. Greveling, H. Wouters, S. R. K. Rodriguez, G. Lehoucq, S. Combrié, A. de Rossi, S. Faez, and A. P. Mosk, *OSA Continuum* **3**(7), 1879-1890 (2020)

3D computational imaging



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Sponsor: NWO TTW-perspectief, Demcon, since May 2021

Supervisors: prof. dr. A.P. Mosk

Computational imaging, Lensless imaging,

My master's thesis project, on sensing off-axis signal within ptychography, was within the field of computational imaging and lensless imaging. For the research project of my Ph.D. I will stay within the computational imaging and lensless imaging field, but focus on 3D imaging using the techniques I've learned before.

After finalising the ptychography project, we will apply a similar style of algorithm as used in that project within 3D computational imaging. This entails solving the inverse problem of reconstruction of the lensless imaging data by creating a model of the system that can be mapped onto a machine learning framework. In ptychography we do this using the automatic differentiation ptychography (ADP) algorithm [1] and we will use this style of algorithm to solve the inverse problem of a DiffuserCam [2].

Furthermore, we will show that the idea of the DiffuserCam can be adopted to do multi or hyper spectral measurements. We will do this using the bayer filter already present in colour cameras, and specifically make use of the wavelength-dependent efficiency of each bayer filtered pixel to distinguish different spectra within a DiffuserCam data-set.

[1] J. Seifert, D. Bouchet, L. Loetgering, and A. P. Mosk, *OSA Continuum* **4**, 121 (2021).

[2] N. Antipa, G. Kuo, R. Heckel, B. Mildenhall, E. Bostan, R. Ng, and L. Waller, *Optica* **5**, 1 (2018).

Laser induced damage control in wafers

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Sponsor:	NWO, ASML, since January 2021
Supervisors:	dr. Dries van Oosten

Optical damage, damage threshold, semiconductor stacks

The field of laser-induced damage on semiconductors is of great relevance to the chip-manufacturing industry. In my research project, I study the mechanisms that play a role in damaging (stacks of) semiconductors. To do this, I aim to find the laser-induced damage threshold (LIDT) as a function of several laser parameters (like wavelength, pulse duration and repetition frequency) for industrially relevant samples. With the lasers that I have at my disposal, I am able to vary these parameters over wide ranges which will allow me to get unique insights into the damage mechanisms.

To study the onset and the different types of damage, I use a variety of imaging techniques. These include optical, interferometry, confocal, scanning electron, transmission electron and atomic force microscopy.

Eventually, I hope to construct theories describing the underlying mechanisms that cause the observed damage. Additionally, I aim to do numerical simulations that reproduce my experimental findings. Finally, I strive to come up with procedures which can be used to prevent laser-induced damage in optical measurement systems.
I do my research in close collaboration with Ester Abram (and her supervisor) at ARCNL and with our sponsor ASML.

Observation and dynamics of discrete time crystal phases in superfluid Bose gases

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Supervisors: prof. Dr. Peter van der Straten

Bose-Einstein condensation, Space-time crystal, Non-equilibrium physics

Discrete time crystals (DTC) are prototypes of non-equilibrium systems, which spontaneously break discrete temporal translational symmetry. In our experiment, such symmetry breaking can be observed in a superfluid quantum gas of sodium atoms, where we demonstrate periodicity both in space and time, by employing a well-controlled drive [1]. The symmetry of the system is spontaneously broken into one of the two Z_2 symmetrical DTC solutions, differing by a phase of π. By utilizing a phase ramping protocol of the drive, a dynamical transition between the two phases can be achieved [2], which we can image and study at a microsecond scale over an extended period, using a dispersive imaging method based on digital off-axis holography [3]. Furthermore, since the symmetry is spontaneously broken with 50-50 percent probability of ending in either solution, our space-time crystal potentially offers rich opportunities of studying two-level quantum mechanical systems and engineering excitations in space and time in the quantum domain [4]. These results can help further evaluate the stability of DTC phases against external perturbations and open a new window of opportunity for studying non-equilibrium phases of matter.

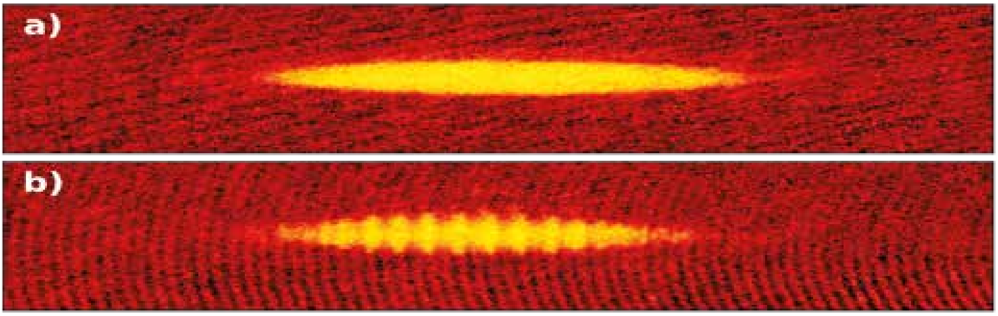
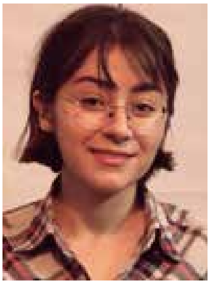


Figure 1: Periodic structure of high-order excitation, which b) appears and a) disappears with twice the period of the drive exciting it. Since both discrete time and spatial symmetry are spontaneously broken, this is dubbed the *space-time crystal*.

[1] J. Smits et al 2020, *New J. Phys.* **22**, 105001
[2] X. Yang, and Z. Cai 2021, *PRL.* **126**, 020602
[3] J. Smits et al 2020, *Opt. Lett.* **45**, 981-984
[4] J. Smits et al 2021, *Phys. Rev. A* **104**, 023318

Label-free detection of action potential in axon



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Sponsor:	NWO, since MAy 2018
Supervisors:	prof. dr. ir. Allard Mosk, prof. dr. ir. Hans Gerritsen

Neuronal activity, SD-OCT, sub-nanometer sensitivity

The transient structural changes accompanying Action potential propagation are still not well understood. Optical methods could detect the mechanical changes such as swelling and shrinkage of neural structures during activity. Such an optical method must detect sub-nanometer change in the neuron which its diameter can be as small as 1μm in mammalian neuronal system and 500μm in giant axon squid. An action potential propagates within 1ms, so to achieve enough sampling rate, this method requires an ultra-fast detector.

In recent years, a number of label free optical techniques based on phase sensitive interferometry have demonstrated detection of neural activity. High sensitivity in measuring changes in optical path length makes these interferometric techniques particularly attractive for detecting potential AP induced nanoscale changes in neuronal optical properties

Spectral-domain optical coherence tomography (SD-OCT) is an effective imaging technique in complex systems. It relies on interference of broadband light rays that are reflected by different parts of the sample. SD-OCT provides simultaneous intensity and interferometric phase information. The intensity of interference yields real-time high resolution (2–500μm) structural images that can be used to select a particular region of interest in neural tissue for functional interrogation. Because of the superior phase stability, sub-nanometre range optical path length change is detectable. With a ultra-fast spectrometer in the SD-OCT setup it can reach a high temporal resolution. Therefore, SD-OCT technology has the time resolution and phase sensitivity to measure the transient structural changes

We have built a setup based on SD-OCT which provides sub-nanometer sensitivity to specific mechanical degrees of freedom. To induce small, controllable deformations of a cellular-scale object we use optical absorption of fluorescent dyes. Some of the excited-state energy is dissipated non-radiatively as heat. The released heat changes the density, volume and refractive index of the object.

We measure expansion caused by heat dissipation during fluorescence in rhodamine B-marked melamine microspheres (diameter 10 μm). Using our SD-OCT setup, we record the change in the optical path length (OPL) while the excitation light is on. Measurement on spheres with and without rhodamine B show that the detected change in OPL is related to absorption properties of rhodamine B not the melamine. The change in optical path length, which we detected with a sensitivity of 0.1 nm, corresponds to the combined effects of change in diameter and refractive index of the spheres.

[1] M. A. Choma *et al.*, *Optics letters* **30**, 1162-1164 (2005)

Imaging Local Ion Concentration Variations by Electric-Double-Layer-Modulation Microscopy

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Sponsor: CSC, since October 2018
Supervisors: dr. Sanli Faez, prof. dr. Allard Mosk

Electric double layer, Ion concentration, Potentiodynamic scattering microscopy

Recently, our group have demonstrated a new optical contrast mechanism for *nonplasmonic* or *dielectric* particles based on periodic modulation of the surface substrate potential[1]. In this method, modulating the EDL close to the surface results in scattering signals that are sensitive to both the local topography and the electrochemical properties of the investigated region. Recent advances in interferometric scattering microscopy and computational modelling of the electric double layer formation indicate that sensing a single surface charge alteration is within technical reach[2].

In this project, we present experimental measurements of the potentiodynamic optical contrast from the nanohole at various electrochemical potentials. Contrary to our previous measurements on transparent ITO substrates, measuring the scattering light from the nanohole allows us to make a direct correlation between the current passing through the inner surface of the nanohole and the observed optical modulation signal, at millisecond timescales. Achieving a simultaneously high temporal and high spatial resolution is essential for filtering out the electrochemical noise caused by surface heterogeneity, in conventional amperometry measurements. Furthermore, this dynamic and correlative measurement allows us to separate the contribution of surface ion absorption to the potentiodynamic scattering signal from that of the diffuse double layer, which in turn can provide new insights into the dynamics of complex surface electrochemical processes.

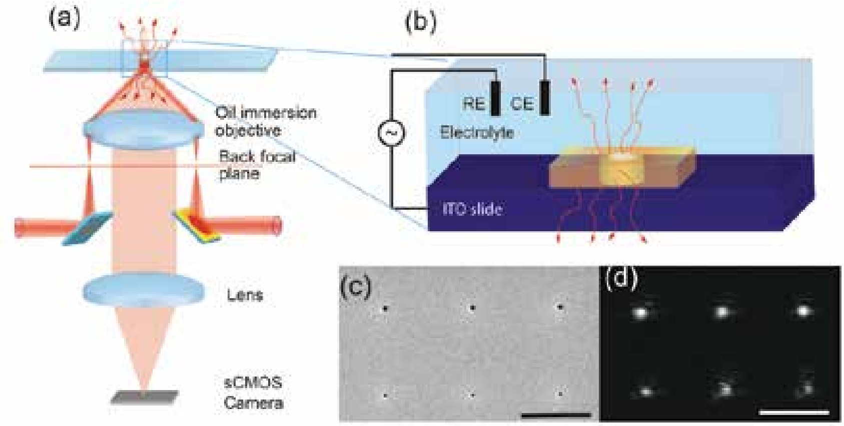


Figure 1: (a) Schematic representation of the experimental setup.(b) Schematic overview of the nanohole sample with potential modulation, the nanohole is drill by FIB in a 100nm thin gold layer which is coated on the ITO or glass slide. (c) SEM image of the nanoholes array (100-20nm in diameter). (d) Scattering light microscope image of the nanoholes array(Scale bars are 5μm)

[1] K. Namink, X. Meng, M. T. M. Koper, P. Kukura, and S. Faez, *Phys. Rev. Applied* **13**, 044065 (2020)
[2] Z. Zhang, J. Yang, C. Lian, and S. Faez, *J. Phys. D: Appl. Phys.* **54**,384005 (2021)


6

ORGANIC CHEMISTRY AND CATALYSIS

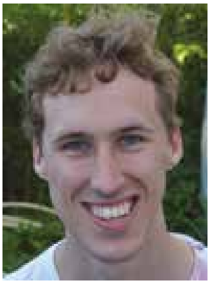
Scientific staff	prof. dr. Robertus Klein Gebbink, prof. dr. Pieter Bruijnincx, dr. Marc-Etienne Moret, dr. Daniel Broere, dr. Arnaud Thevenon
Emeritus	prof. dr. Gerard van Koten
Technical support	dr. Thomas Ran, dr. Leon Witteman, dr.Johann Jastrzebski
Administrative staff	Silvia Benschop
PhD students/Postdocs	24

Research Mission

The synthesis of chemical building blocks and new organic compounds with interesting physical, biological, or pharmaceutical properties remains as a challenge for the chemist. Recent and ongoing developments specifically ask for 'clean' and efficient synthesis protocols, preferably based on renewable resources, to be developed for current and future applications. Catalysis plays an important role in the development of such 'clean' and sustainable synthetic protocols.

The OCC research group is actively involved with various aspects of catalysis. New organometallic and coordination complexes are designed and synthesized in search of new catalytic properties in, e.g., oxidation catalysis or in the catalytic conversion of biomass. In the design of new catalysts and new catalytic procedures the active sites of metallo-enzymes play an important inspirational role. In addition, new concepts in ligand design are pursued, e.g. through the development of cooperative and dinucleating ligands, and the design of ligands based on less traditional donor atoms like Si. Furthermore, research is done at the interface of organic and inorganic chemistry, that is on the design of homogeneous as well as heterogeneous catalyst systems that will be used in catalytic organic syntheses and the chemical transformation of renewable feedstocks, such as biomass, CO2 and recycle or waste streams.

Combining metal-metal cooperation and metal-ligand cooperation in CO_2 activation



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Organometallic chemistry, Metal-ligand cooperativity, CO_2 activation

Various metalloenzymes feature cofactors with a multinuclear assembly of base metals that catalyze challenging chemical transformations at ambient conditions.[1] However, synthetic homogeneous catalysts rely on one metal, often a noble metal, surrounded by a ligand. Inspired by nature's remarkable multinuclear enzymes, our group is motivated to synthesize and use bimetallic systems in homogeneous catalysis. The ligand system we are exploring are so-called PNNP 'expanded pincer' ligands, that can bind two metals in close proximity.[2] This arrangement can allow cooperative substrate binding and activation by both metal centers, a concept that has led to a new catalytic transformation with a dinickel system.[3]

In this project the coordination chemistry of the PNNP ligands with various transition metals (Fe, Cu and Ru) is studied. We study the complexes' coordination chemistry to gain a better understanding of the reactivity of the synthesized bimetallic systems. Additionally, the fundamental bond activation processes and reactivity are studied using both spectroscopic techniques and DFT methods. The aim of this project is the use of these bimetallic complexes as catalysts for the reduction of CO_2 to enable its use as a C1-building block. In nature CO_2 is used as C1-building block by the enzyme carbon monoxide dehydrogenase (CODH) using a multimetallic nickel/iron cofactor in combination with protons and electrons.[1] Therefore, we envision the same use of CO_2 as non-toxic, renewable C1-building block using our bimetallic complexes as catalysts.

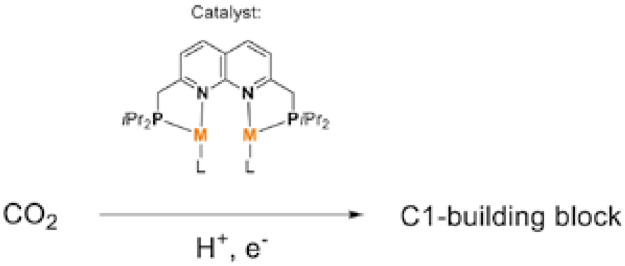

Figure 1: The aim of using CO_2 as a C1-building by its reduction using bimetallic PNNP complexes as catalyst.

[1] Armstrong & Ragsdale *Chem. Rev.* **114**, 4149-4174 (2014)
[2] E. Kounalis et al., *Chem. Eur. J.* **25**, 13280-13284 (2019).
[3] Y-Y. Zhou & C. Uyeda *Science* **363**, 857-862 (2019).

Early-Late transition metal complexes bearing naphthyridine-based ligands

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Organometallic chemistry, Homogeneous catalysis, (Hetero)Multinuclear complexes

Nature frequently uses the intricate interplay between metals to tackle challenging transformations. An interesting example where this strategy is employed, is that of Carbon Monoxide Dehydrogenase (CODH). This enzyme contains a Ni-Fe cofactor that allows the interconversion of CO and CO_2, demonstrating how having multiple metals in close proximity facilitates activating challenging bonds. Moreover, it shows that employing two different metals allows for different and new kinds of reactivities, expanding upon chemical space.

Motivated to translate this reactivity towards synthetic systems, the pursuit of this project is to design ligands that are capable of binding different metals close to each other. Specifically, the highly polarised interactions between early and late transition metals will be probed, with the aim to gain a fundamental understanding of these interactions but also to explore if this polarisation can be transferred to small molecules for applications in catalysis. The naphthyridine moiety has been found to be a suitable, rigid scaffold that allows the binding of two metal centres close to each other.[1-4] For this, the pendant donors that flank the naphthyridine have a defining influence on the type of metals that can be bound, dictating the geometry around each metal centre and largely influencing the steric and electronic properties. As such, throughout this project, suitable donor-metal matches must be explored. To achieve this, homonuclear Early-Early transition metal complexes and homonuclear Late-Late transition metal complexes with naphthyridine-based ligands will be synthesised first. Then, with the knowledge obtained from these complexes, new naphthyridine-based ligands with a mixed donor set can be made to support heterometallic complexes. With these complexes in hand, fundamental insights can be obtained that can be used for the development of heterodinuclear catalysts for sustainable chemical transformations.

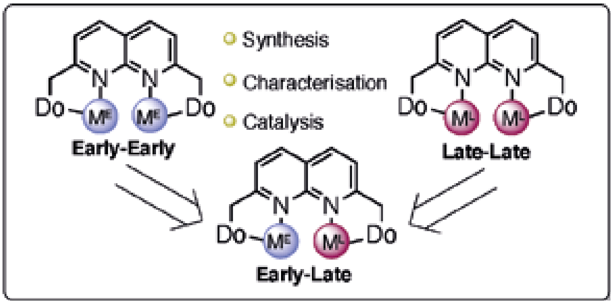

Figure 1: Graphical representation of the aims of this project.

[1] E. Kounalis *et al.*, *Chem Eur J* **25**, 13280-13284 (2019)
[2] T.C. Davenport *et al.*, *Dalton Trans* **44**, 12244-12255 (2014)
[3] YY. Zhou *et al.*, *Inorg Chem* **53**, 11770-11777 (2014)
[4] E. Kounalis *et al.*, *Organometallics* **39**, 585-592 (2020)

Epoxidation and site-selectivity oxidation by deuterated bulky non-heme iron catalysts: improving catalytic lifetime and site-selectivity

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Iron complexes, Aliphatic oxidation, Epoxidation

Site-selective oxidation of aliphatic C-H bonds and the epoxidation of C=C bonds are relevant to organic synthesis. It was found that modifying the N2Py2 ligand with bulky tri-isopropylsilyl (TIPS) substituents at the pyridyl donors leads to an overall enhancement in substrate conversion and yield of the region selected product.[1-2] Although this ligand modification provides a powerful handle to improve the selectivity and catalytic efficiency of these non-heme iron catalysts, their lifetime remains an issue.[3-4] One way to improve catalyst lifetimes is the installment of deuterium atoms on the 2-pyridinyl methylene site was found some interesting effects on catalyst lifetimes in catalytic oxidations using iron N2Py2 catalysts.

Therefore, two new deuterated bulky iron complexes that combine two effects, 1) TIPS (bulky) catalyst and 2) deuterated catalyst, were prepared and used for catalyzing 11 typical substrates and one challenging substrate. As a consequence, the deuterated bulky complexes show an excellent improvement in regioselectivity oxidation of aliphatic C-H and epoxidation of C=C bonds.

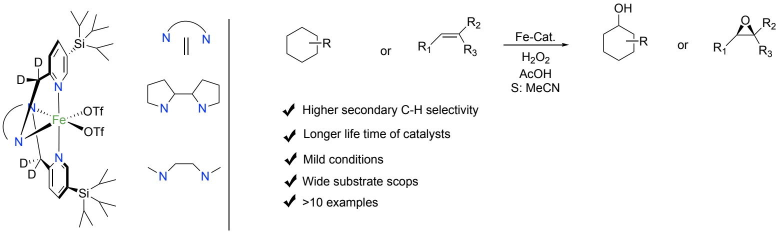

Figure 1: The structure and application of iron complexes

[1] D. Font *et al.*, *Angew. Chem. Int. Ed.*, **55** (19), 5776-9 (2016)

[2] O. Cusso *et al.*, *J. Am. Chem. Soc.*, **138** (8), 2732-8 (2016)

[3] J. Chen, *et al.*, *ACS Catal.*, **9** (4), 3564-3575 (2019)

[4] Z. Codola *et al.*, *J. Am. Chem. Soc.*, **141** (1), 323-333 (2019)

A mulstiscale catalysis and engineering approach to CO_2-to-X

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Catalysis, Circular Economy, Carbon Dioxide

In the Paris Agreement the IPCC determined that the release of greenhouse gases in our atmosphere must be reduced, with CO_2 being the most important one. Since the start of the industrial revolution in the 19th century the CO_2 concentration in ambient air has increased from 280 ppm to more than 400 ppm. Large amounts of CO_2 are emitted by sectors such as the cement and coal industry, where CO_2 is emitted in concentrations of 10 – 30 %. Using the CO_2 emitted at such point sources, e.g. by catalytic conversion with renewable energy, as carbon feed can result in the synthesis of CO_2 neutral, or better yet, negative, products and fuels. This comes with considerable challenges in terms of (combining) purification, capture and conversion of the CO_2 feed. In this project, we aim to develop new (integrated) catalytic conversion and reactor technology for the conversion of CO_2 to chemical building blocks. The usage of both conventional and novel scrubbing agents in novel combinations with homogeneous and heterogeneous catalysts are researched in combination with the appropriate reactor design. Target molecules in the aforementioned processes are e.g. methanol and formates, which can be used both as chemical building blocks and as hydrogen carriers for renewable fuels. A second approach is the combination of the capture and conversion functions in one material with e.g. triazine based solid chemicals. During this project the effect of the concentration and purity of the gas stream on the process efficiency will be determined, as well as the possibility to operate the system in continuous flow using e.g. microfluidics or bubble reactors. Figure 1 depicts the process of carbon capture, conversion and the subsequent combustion, creating a closed carbon cycle.

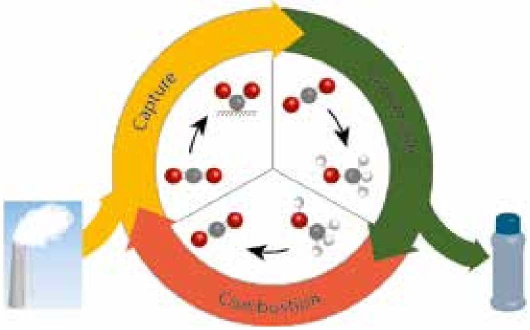

Figure 1: Carbon dioxide can be captured from the industry and subsequently converted to form chemical building blocks and fuels. Burning these materials and capturing the CO_2 results in a circular economy.

Upcycling of waste-sourced feedstocks into chemicals

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Upcycling, Circular chemistry, Catalysis

Currently, we are rapidly exhausting the Earth's resources, using more than what can be provided for in an ecological way. Indeed, to live more sustainably we need to make haste with both the energy- and resource transition. This requires us to close the carbon loop and shift to a circular society. In the energy- and transportation sector, fossil resources can be replaced by renewable electricity, and, in part, biofuels. However, our material needs also rely heavily on carbon. Carbon circularity therefore is an important objective for a sustainable chemical industry and can be achieved by using either CO_2 or biomass for virgin production and by turning waste into a resource to produce chemicals.[1]

In fact, growing populations in urban areas produce increasing volumes of aqueous municipal waste streams, a major issue that calls for improved waste management. Current wastewater recycling is energy intensive and results in the loss of the valuable resources accumulated in the sewage sludge, which is mainly disposed through composting, landfilling or incineration.

Research aimed at recovering and upgrading such carbon streams to value-added chemicals sustainably with efficient and clean conversion processes, will aid our transition to a circular society[2]

In this project, we aim to develop novel strategies that enable the catalytic transformation of wastewater-sourced carbon feedstocks into valuable chemical building blocks. Compared to many current microbial strategies e.g., waste to biogas, this provides structures of increased chemical complexity and importance for novel circular value chains.

[1] K. Kümmerer *et al.*, *Science* **367**, 369-370 (2020)
[2] T. Keijer *et al.*, *Nat. Chem.* **11,** 190-195 (2019)

Mapping lignin property space through molecular size selection and chemical modification

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Green chemistry, Organic synthesis, Spectroscopy

Lignin is one of the key structural components of the plant cell wall and is the most abundant naturally occuring form of aromatic carbon on Earth.[1] It also is one of the major waste products from the paper and pulping industries, with most being burnt solely to produce or power for the biorefining or pulping which liberates the lignin from the desired carbohydrate material. Structurally, lignin is comprised of highly functionalised polyphenolic chains, which presents potential as a lucrative feedstock for oxygen rich building-block molecules, or as a platform material for use in complex biopolymers.

The aims of my research are to provide insight on the choice of lignins for a selected application by establishing property maps that link key application performance indicators to structural characteristics (eg. molecular weight and particle size, functional group identity/distribution, degree of condensation). Fractionation of a diverse set of technical lignins reduces sample heterogeneity and polydispersity, allowing for comparison of the fractions to the whole samples. Covalent functionalisation of the fractions facilitates control and expansion of the lignin property space, solidifying the correlations between structure and property. A range of modification methods are employed, from simple esterification, to more complicated catalytic processes.

Extensive characterisation of each fraction and modified sample provides a large analytical burden. A chemometric toolbox is therefore being developed for rapid characterisation with IR spectroscopy and multivariate analysis. Quantitative, correlative approaches are used to elucidate the underlying modification-property relationships within the lignin property maps. The underlying aim is to study the property maps, rather than the specific application performance of the samples, as one or more properties can serve as key performance indicator(s) for a variety of applications. The maps should effectively provide deep insight which will indicate the performance of the lignin, allowing for the industrial partner to match a desired application with the best suited lignin.

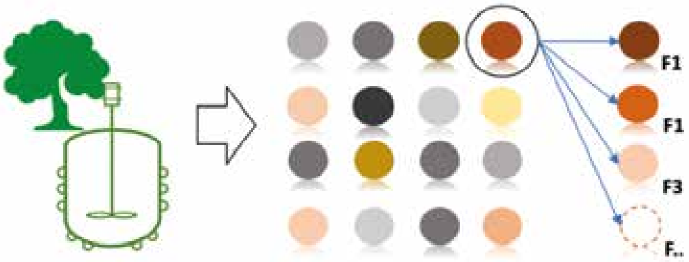

Figure 1: The conversion of biomass to discrete fractions with improved property homogeneity

[1] R. Rinaldi *et al.*, *Angew. Chem.*, **55**, 109, 8164–8215 (2016)

Polyolefin upcycling and cleavage through selective catalytic (oxy)functionalization

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Chemical recycling, Polyolefins, C-H activation

To add value to overall chemical recycling schemes, there is a need for upcycling of part of the circular polymer stream, e.g. by targeting smaller-volume, higher functionality monomers or polymers other than the original ones. This post-polymerization modification (PPM) requires selective introduction of functional groups into the backbone of waste polymers, functional groups that endow the polymers either with new properties or with reactive handles that can be modularly addressed, or, alternatively handles that facilitate C-C bond cleavage and depolymerization.[1] Many catalytic routes have been developed in the past years for selective (late stage) C-H activation on small molecules, approaches that now can be translated to modification of polyolefins.[2]

In this project we aim to connect post-polymerization modification (PPM) of commodity polyolefins with selective oxyfunctionalization of C-H bonds by non-noble metal based oxidation catalysts. During this project we will study the effect of the nature, density and distribution of introduced functional groups on the physiochemical properties.

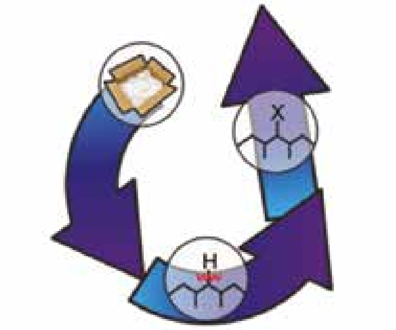
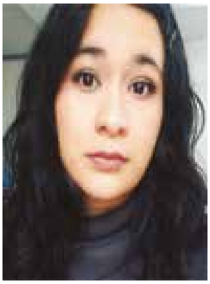


Figure 1: Polymer upcycling via post-polymer modification (PPM).

[1] J.B. Wiliamson *et al.*, *Angew. Chem. Int.* **58**, 8654-8668 (2019)
[2] M.C. White *et al.*, *J. Am. Chem. Soc.* **140**, 13988-14009 (2018)

Divergent reactivity of a nickelacyclobutane



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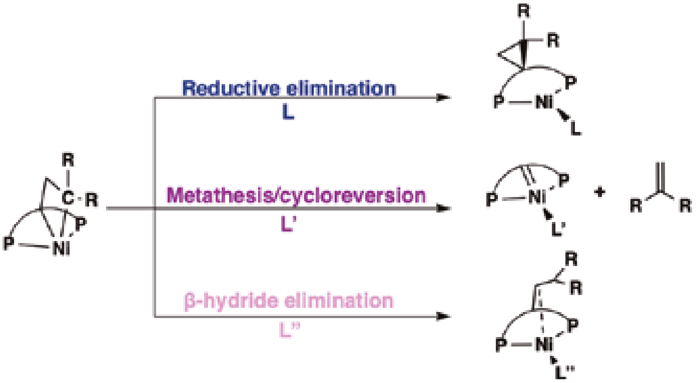
Metallacyclobutanes, Metal carbenes, Organometallic chemistry.

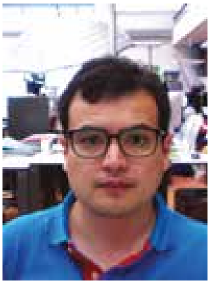
Metallacyclobutanes are important reactive intermediates present in catalytic cycles such as olefin metathesis and cyclopropanation.[1,2] They can undergo reductive elimination yielding cyclopropane derivatives or cycloreversion and β-hydride elimination yielding different types of alkenes (Scheme 1).[3,4] However, a general understanding of what governs their reactivity towards each route is lacking. For nickel, early studies reported the influence of the coordination number of the nickel center in the major product of decomposition of nickelacyclobutanes by the identification of the resulting organic products. It was suggested that transient pentacoordinated nickelacycles enhanced the formation of metathesis products, an uncommon pathway for nickel complexes.[4,5]
In this research, we use nickel complexes featuring a PC=CP type ligand to trap reactive intermediates such as a nickel carbene. The resulting nickelacyclobutane is stable in weakly coordinating solvents allowing isolation and characterization. The nickelacyclobutane depicts an unusual pentacoordinated structure and its reactivity can be directed depending on the presence and nature of exogenous ligands in the reaction medium, yielding selectively products of either cyclopropanation, metathesis, or β-hydride elimination. With the help of DFT calculations, the factors controlling the selectivity of nickelacyclobutane decomposition are investigated.



Scheme 1. Decomposition routes of a nickelacyclobutane in a pincer ligand framework.

[1] J. Smith *et al., Nature* **109**, 640-645 (2013)
[1] R. H. Grubbs, A. Miyashita, *Fundam. Res. Homog. Catal.* Springer US, Boston MA, 207-220 (1978)
[2] O. M. Ogba, N. C. Warner, D. J. O'Leary, R. H. Grubbs, *Chem. Soc. Rev.*, **47**, 4510-4544 (2018)
[3] J. Campora, P. Palma, E. Carmona, *Coord. Chem. Rev.*, 207-281 (1999)
[4] R. H. Grubbs, A. Miyashita, *J. Am. Chem. Soc.*, **100**, 7418-7420 (1978)
[5] A. Miyashita, M. Ohyoshi, H. Shitara, H. Nohira, *J. Organomet. Chem.*, **338**, 103-111 (1988)

Nickel catalyzed cross-coupling mechanistic studies: The crucial role of a PPP pincer ligand.



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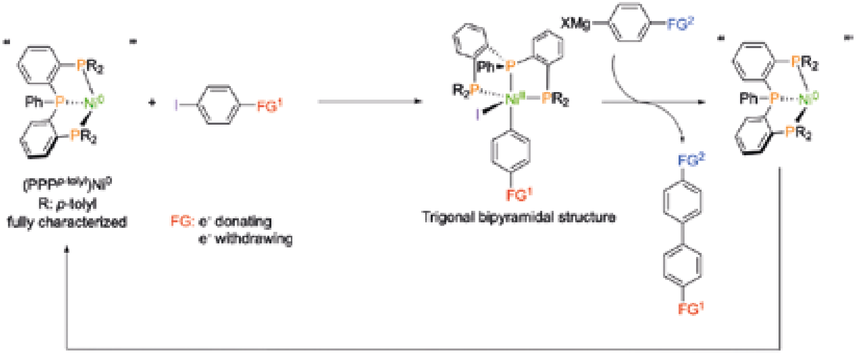
Cross-coupling, Nickel, Mechanism

Cross-coupling reactions catalyzed by transition metal complexes are ubiquitous synthetic tools in academic and industrial research. The versatility of aryl Grignard reagents makes Kumada coupling an essential category among the cross-coupling methodologies. The use of nickel-based catalysts instead of palladium ones goes beyond sustainability justifications. Nickel shows a higher activity to activate challenging chemical bonds such as aryl chlorides or aryl ethers. Nevertheless, nickel has access to open-shell oxidation states such as Ni^I or Ni^{III} leading to radical off-cycle pathways. A throughout mechanistic understanding is then required for the design of efficient nickel-based catalysts.

My research aims to study the mechanistic study of the cross-coupling process of aryl-halides with aryl Grignard reagents catalyzed by well-defined nickel precatalysts bearing a pincer $PPP^{p\text{-tolyl}}$ ligand. The unique coordination framework offered by this ligand allowed us to identify and characterize key Ni^0 and Ni^{II} intermediates for the cross-coupling process. Furthermore, our pincer ligand also enables us to characterize Ni^I off-cycle species and understand their formation. We hope that our studies will contribute to paving the way for future catalytic coupling applications of tridentate phosphine nickel complexes, which are still largely unexplored.



[1] Pérez-García *et al.*, *Organometallics* **39**, 1139-1144 (2020)

[2] Pérez-García *et al.*, *CHIMIA* **74**, 495-498 (2020)

Exploring the reactivity of a strained silanide cage towards its use as organocatalyst

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Silicon compounds, Amphoteric lewis character, Organocatalyisis

Most homogeneous catalysis is based on transition metal complexes. However they can be difficult to synthesize, potentially toxic and expensive. So bond activations by main-group compounds is of considerable interest. Frustrated Lewis Pairs (FLPs) possess an amphoteric Lewis character, which means that they bear both an available acceptor orbital (empty orbital) and a donor orbital (lone pair electron) that mimic a similar function of the frontier orbitals in transition metal complexes which allows the activation of small molecules. Some species that also have Lewis amphoteric character are Si (II), Ge (II) and Sn (II) species in which usually the acidic and basic character are in the same atom, moreover this species present a narrow HOMO-LUMO gap, that allows metal-free bond activation and in some cases catalysis [1,2] Low-valent silicon(II) compounds, like silylenes, are emerging as ligands for transition metals for their use in homogeneous catalysis. However, they are also interesting for their use in the activation of small molecules. Silanides, ([R3Si-]), are anionic low-valent silicon (II) compounds with a lone pair at the silicon center with a counteranion that compensate the negative charge. They are difficult to isolate as free compounds and are usually mostly observed as intermediates in reactions involving silicon, consequently their reactivity is less studied compared to other Si(II) compounds. [3,4] In our group we recently showed that a silanide zwitterionic cage when protonated acts as a strain-release Lewis acid. In this process, the Si center sequentially acts as a nucleophile (base) and then as an electrophile (Lewis acid) to facilitate the activation of two relatively unreactive molecules, suggesting the potential of such cage compounds as biphilic main-group centers.[5]

In this context we are studying the reactivity of an all-organic, free silanide in the activation of small molecules and investigating how the strain of the cage influences the reactivity.

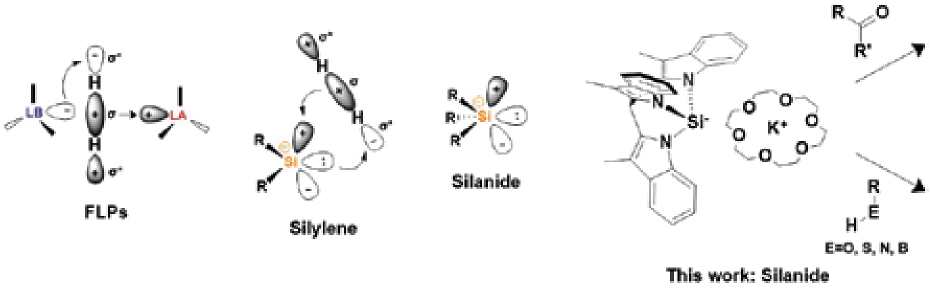

Figure 1: a) FLP H2 activation b) Si(II) H2 activation. c) Silanide d) this work silanide activation of small molecule

[1] Stephan D., *Acc. Chem. Res.*, **48**, 306-316 (2015)

[2] Hoge *et al. Angew. Chem. Int. Ed.* **60**, 2-10 (2021)

[3] Benedek, Z. and Szilvási, T., *RSC Adv.* **5**, 5077–5086 (2015);

[4] Witteman, L. *et al. Chem. Eur. J.* 24, 12236–12240 (2018).

[5] Moret *et al. Angew. Chem. Int. Ed.*, **60**, 2 – 11(2021)

Synthesis of dinuclear earth-abundant ‘expanded’ pincer complexes and exploration of their catalytic properties

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Dinuclear complexes, Organometallic chemistry, Homogeneous catalysis

Traditional homogeneous catalysis has largely relied on the use of mononuclear complexes as catalysts, in contrast to catalytic sites in enzymes which are often multinuclear. Since these enzymes have catalytic properties that are unrivaled by synthetic systems, we are interested in exploring the use of bimetallic complexes in catalysis. Our complexes bear an ‘expanded’ PNNP pincer ligand, which is able to coordinate two metal centers in close proximity.[1] This allows for cooperative reactivity between these metal centers, which has been shown to enable unprecedented catalytic reactivity in related systems.[2]

The focus of this project is to synthesize new dinuclear complexes with first row transition metals (Cu and Co) to study how their nuclearity influences their reactivity. We are studying a dicopper hydride complex in the catalytic hydrosilylation of ketones (Figure 1). Hydrosilylation is a well-studied reaction for reported copper hydride complexes.[3] Thus far, experimental studies indicate that our complex follows a novel mechanism, not previously observed for copper hydride species. In addition, DFT methods are employed to investigate the electronic structure of our complexes, for example in a dicobalt complex that binds two equivalents of diethylsilane (H_2SiEt_2). NBO as well as QTAIM calculations indicate that this complex has a silylene like structure with a Co–Co interaction. Currently, we are looking into experimental support for the electronic structure and to correlate this structure with the observed reactivity. The goal is to gain better understanding of the properties of dinuclear complexes and how these can be exploited for the catalytic transformation of biomass derived aromatics into high value chemicals.

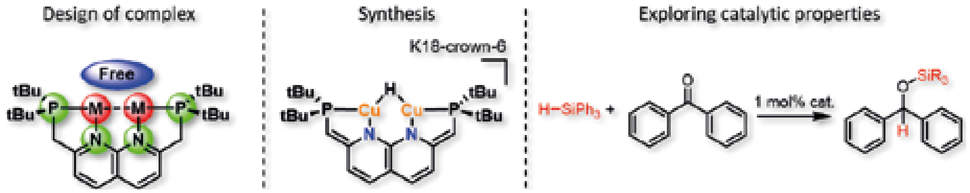

Figure 1: Design of bimetallic PNNP complexes (left), the synthesized anionic dicopper hydride complex (middle) and the hydrosilylation of bulky ketones catalyzed by this anionic PNNP dicopper hydride complex (right).

[1] E. Kounalis *et al.*, *Chem. Eur. J.* **25**, 13280-13284 (2019)
[2] Y-Y. Zhou and C. Uyeda *Science* **363**, 857-862 (2019)
[3] S. Díez-González and S. P. Nolan, *Accounts of Chemical Research*, **41**, 349-358 (2008)

Structured hydroxyapatites composites as efficient solid base catalysts for liquid and gas phase condensation reactions

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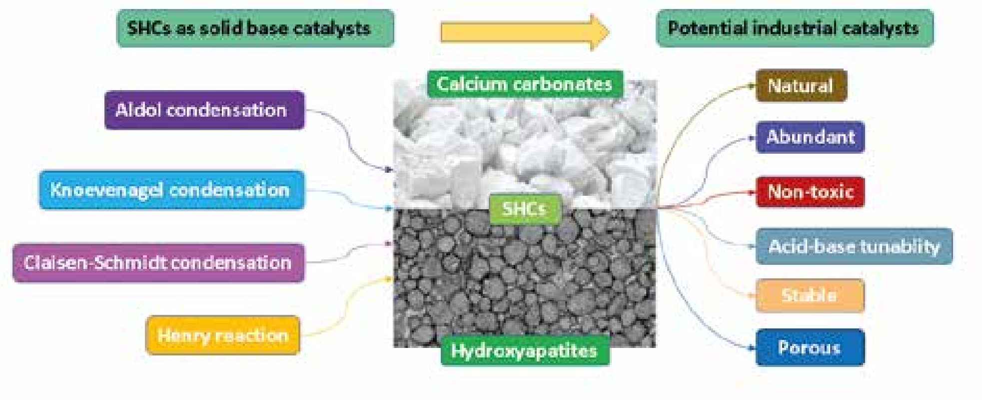
Supervisors: prof. dr. Pieter Bruijnincx

Solid base catalysts, Biomass conversion, Condensation reactions

The research project is divided into 2 main packages, encompassing the leverage of structured hydroxyapatite composites (SHCs) as efficient solid base catalysts for liquid and gas phase biomass upgrading through condensation reactions. Catalytic condensation reactions are an important tool to upgrade platform chemicals by C–C bond formation to give higher value products used for applications ranging from transportation fuels to fine or specialty chemicals. Recently, condensation reactions have become even more significant as a tool to upgrade bio-derived feedstock, offering the opportunity to produce longer carbon chain products with high atom economy and with limited generation of (harmless) by-products.

SHCs are mixed mineral morphologies consisting of the core of calcium carbonates (CC) and a shell of lamellar hydroxyapatites surrounded by agglomerated fine CC particulates. In the first package, we reported the usage of SHCs as highly efficient and recyclable solid base catalysts for various liquid phase condensation reactions (Scheme 1). In the second package, reports the effectiveness of carrying out the gas phase Guerbet reaction of ethanol (EtOH) to n-Butanol (BuOH) over SHCs as efficient solid base catalysts. These SHC catalysts were examined in a continuous flow reactor, and were found to catalyze the dehydrogenation, aldol condensation and hydrogenation steps of the Guerbet reaction converting EtOH to BuOH. In general, these highly active solid base catalysts, of which the acid–base and morphological properties can be carefully tuned, provide a promising new addition to the existing portfolio of industrially employed solid base catalysts.



Scheme 1: SHCs as solid base catalysts for various condensation reactions

7

SOFT CONDENSED MATTER AND MOLECULAR BIOPHYSICS

Scientific staff	prof. dr. Alfons van Blaaderen, prof. dr. ir. Marjolein Dijkstra, dr. Arnout Imhof, dr. ir. Marijn van Huis, prof. dr. René van Roij, dr. Laura Filion, dr. Gerhard Blab, dr. Freddy Rabouw, dr. Lisa Tran
Adjunct staff	dr. Patrick Baesjou, dr. Krassimir Velikov, dr. Michiel Hermes
Technical support	Peter Helfferich, Chris Schneijdenberg, Relinde van Dijk-Moes, Dave van den Heuvel, Elleke van Harten
Administrative staff	Hester van der Putte, Mijke Heldens, Mirna Marrink (manager a.i.)
PhD students/Postdocs	29

Research Mission

The emphasis is on the development and (spectroscopic) characterization of colloids and nanocrystals as well as on the manipulation and 3D real-space analysis of their self-assembly. Motivation comes both from the use of these systems as condensed matter model systems, and from their use as advanced materials in applications like photonic crystals and electronic-ink. In addition, we perform computer simulations and theory on soft condensed matter systems and try to bring these together with the experiments in a strongly synergistic approach.

Molecular Biophysics: The group develops and exploits fluorescence spectroscopy based techniques in microscopy. Fluorescence and different Electron Microscopy techniques are combined to obtain information at the highest possible resolution. The novel methodologies utilize advanced detection methods, contrast based on fluorescence spectroscopy and integration of optical and electron microscopy in one setup. Luminescent labels that can be visualized in both fluorescence and electron microscopy are developed and characterized. These developments are driven by biological and biophysical problems which cannot be addressed with conventional imaging techniques.

Extending *in situ* liquid phase transmission electron microscopy to etching of silica, polymer microgels and ion exchange

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Supervisors: prof. dr. Alfons van Blaaderen, dr. ir. Marijn van Huis
Liquid phase EM, Silica, PNIPAM

Liquid phase electron microscopy (LP-EM) consists in imaging microvolumes of liquid with conventional electron microscopes, thus allowing the observation of liquid dynamics and processes at the nanoscale. Since the interior of electron microscopes is held at high vacuums, silicon-chip architectures sealing the sample from the vacuum environment are employed. LP-EM has some limitations, such as electron beam-sample interactions and consequences.

In this project several systems have been and are currently studied in the LP-EM set-up.

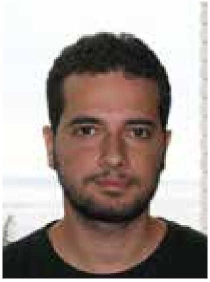
Firstly, silica etching in basic aqueous media was studied. A particular type of silica nanospheres (Amino Acid Catalyzed silica-based synthesis) was used to establish beam-sample interactions and their influence on the etching process. Then optimal imaging conditions were determined and applied to many silica and nanoparticle@silica core-shell model systems.[1,2]

The second challenge we tackle is the direct imaging of unlabelled polymeric colloidal particles in water. In particular, we intend to image unlabelled poly(N-isopropylacrylamide) colloidal spheres. We are currently exploring many strategies to generate contrast in our samples to image systems otherwise impossible to image without labelling.

Finally, we are pushing to image, for the first time, ion exchange processes happening in liquid-phase at the nanoscale. More precisely, we focus on metal chalcogenide nanoparticle systems. This process remains elusive to imaging, given the strong effects of the electron beam in our samples. Liquid media used in ion exchange processes are typically rich in cations that reduce and electron beam illumination, resulting in undesired beam-induced metal nanoparticle formation. We currently work towards imaging but also reducing such undesired effects.

[1] A. Grau-Carbonell *et al.*, *ACS Applied Nanomaterials* **4**, 1136-1148 (2021)
[2] S. Sadighikia *et al.* , *Nano Select* **2**, 313-327 (2021)

Tracking interactions from particles' trajectories



Alberto Giacomo Orellana, a.g.orellana@uu.nl
Sponsor: Utrecht University, since October 2019
Supervisors: dr. Laura Filion, Prof. dr. Marjolein Dijkstra

Monte Carlo simulations, Molecular dynamics, Pair distribution function

We studied two different methods that try to predict the interaction between particles, one based on the radial distribution function[1] while the other is based on particle trajectories.[2] We compare the results for different values interaction strengths, densities and time steps for four different models: Lennard Jones, Yukawa, Morse and Soft Spheres. Both methods show a good agreement between the true interaction potential and predicted numerical one for the four potentials. However, the accuracy of the trajectory method is strongly depending on how short the time between snapshots along the trajectory is. We also successfully extend the method of particles trajectories[2] for anisotropic interactions, the method has been applied to aligned dipole system with good agreement between theory and simulations.

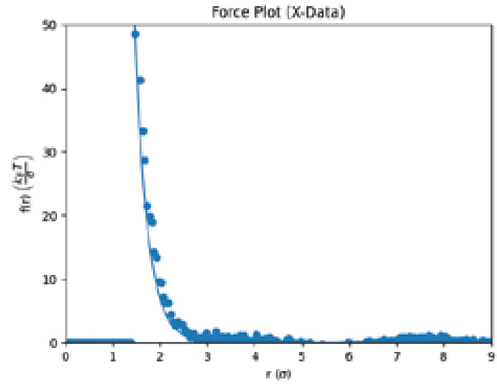


Figure 1: Results obtained with the trajectory method vs theoretical value of the force.

[1] Stones *et al.*, *Phys. Rev. Lett.*, **123.9**, 098002 (2019)

[2] Jenkins *et al.*, *Soft matter* **11.35**, 6948-6956 (2015)

Inverse design of free-energy landscapes for colloidal self-assembly of target phases

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Inverse design, Enhanced sampling, Machine learning

Self-assembly represents a promising route to synthesize nanomaterials with desired mechanical, electronic and optical properties. However, precise control of such ordering and aggregation processes remains a daunting task. Computational inverse design is currently paving the way to efficiently create self-organizing materials.[1] My research is focused on applying evolutionary computation to, first, reverse-engineer the stability of a target phase and, second, sculpt its surrounding free-energy landscape. That is, in finding design parameters—i.e., thermodynamic conditions and interaction potentials for a given system—that yield a specific stable crystal structure, as well as preferred transition pathways and free-energy barriers from and to other metastable states. The parameter optimization is performed by algorithms that require a fitness or objective function. We define a fitness based on local order parameters[2] or on deep-learning classifiers based on diffraction patterns.[3] However, this strategy will only be practical if the target phase can be assembled within an affordable simulation time. To overcome this problem, we are currently integrating enhanced-sampling strategies into the design pipeline. We can then redefine the fitness as the free energy of the target phase with respect to a reference, or as the shape of the minimum free-energy pathway toward the target phase in the space of certain order parameters. The order parameters for these free-energy calculations can be defined based on local environments[4] or processed by deep-learning models.[5] Moreover, free energies can also be extracted from normalizing flows[6], and interaction potentials can be parametrized based on machine learning.[7] Our design pipeline provides a robust tool to control not only stable phases, but also transition pathways and metastable states of complex colloidal systems.

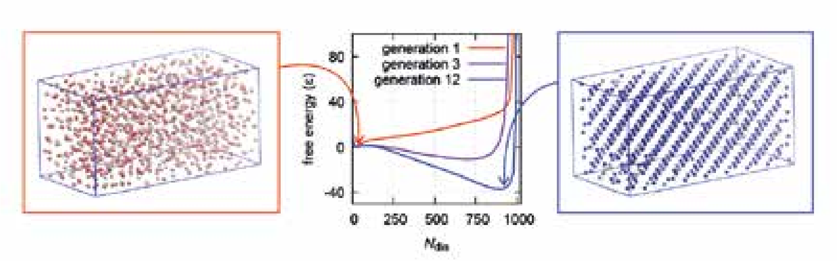

Figure 1: Representative fluid-to-diamond free-energy profiles during the optimization of a stable diamond phase.

[1] M. Dijkstra *et al.*, *Nature Materials* **20**, 762–773 (2021)
[2] R. Kumar *et al.*, *J. Chem. Phys.* **151**, 084109 (2019)
[3] G.M. Coli *et al.*, *arXiv*:2106.14615 (2021)
[4] P.M. Piaggi *et al.*, *J. Chem. Phys.* **152**, 204116 (2020)
[5] J. Rogal *et al.*, *Phys. Rev. Lett.* **123**, 245701 (2019)
[6] F. Noé *et al.*, *Science* **365**, 6457 (2019)
[7] F. Musil et al., Chem. Rev. 121 9759-9815 (2021)

Manipulating cellulose nanocrystal self-assembly

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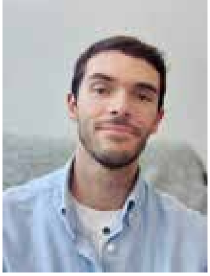
Sponsor: SCMB, January 2021
Supervisors: prof. dr. Alfons van Blaaderen, dr. Lisa Tran

Cellulose nanocrystals, Structural color, Liquid crystals



Aqueous suspensions of cellulose nanocrystals (CNCs) have recently risen into focus due to their ability to self-assemble into a lyotropic, cholesteric liquid crystalline phase. These rod-like colloids are commonly obtained from the acid hydrolysis of most cellulose sources using sulfuric acid. This process also negatively charges the CNC surface, granting them significant stability in aqueous suspensions. An intriguing property of these suspensions is their ability to retain this cholesteric structure during water evaporation. During evaporation, the cholesteric structure is compressed, ultimately yielding a solid film with photonic responses in the visible. The resulting structural colour can be tuned by several means through manipulation of the cholesteric pitch in the final film, which is proportional to the reflected colour's wavelength.

Pitch size manipulation has recently been reported in CNCs decorated with superparamagnetic iron nanoparticles (mCNCs), by applying external magnetic fields of the milliTesla range.[1] The self-assembly mechanisms of CNCs in suspension remain to be fully elucidated, and magnetically doping CNCs will enable the use of weak, external fields in manipulating the CNC assembly. Investigating the morphology of the magnetic dopants will additionally provide insight on the influence of particle geometry on the end cholesteric structure.

My project aims to further explore the effect of particle geometry and magnetic doping on liquid crystalline self-assembly, opening doors to the enhanced control of CNC self-assembly that is essential for the production of sustainable, structurally coloured paints.

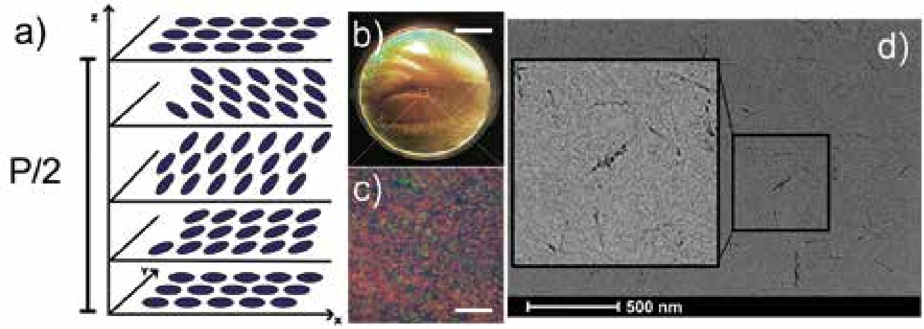


Figure 1: a) Diagram of a cholesteric structure, representing the distance equivalent to a half-pitch; b) photograph of a solid CNC film, produced from evaporation in a polystyrene petri dish over 10 days; c) microscope image, in reflection mode, of a red portion of the CNC film; d) TEM image of CNCs doped with magnetic iron oxide nanoparticles. Scale bars are b) 1 cm and c) 500 μm.

[1] T. Chen *et al.*, *ACS Nano* **14**, 9440-9448 (2020)

Confined colloidal liquid crystal defect formation and dynamics

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Sponsor: SCMB, since March 2021
Supervisors: dr. Lisa Tran

Liquid crystals, Colloids, Topological defects

Rod-like particles demonstrate liquid crystalline (LC) phases, from the molecular to macro-scale. The nematic LC phase, as found in displays, is described as having long-range orientational order, whilst still being able to flow (Figure 1(a)). Molecular LCs over the last half-century have revolutionized the display industry and have been proposed for a multitude of innovative technologies.

Attention has turned to include observations of LC behavior in biological systems, with specific interest in the mediation of processes through topological defect formation and dynamics. Epithelial tissue cell death and extrusion has been linked to the defect dynamics of the system (Figure 1(b)).[1] These biological nematics typically have complex confinement, with micron-sized or larger particles, and exhibit activity. The understanding of orientational control and defect dynamics with complex geometrical confinement is incomplete for passive and active nematics. As such this lack of understanding is a major challenge in the discernment of the underlying mechanisms involved in these biological systems.

My research aims to bridge this knowledge gap by developing a model experimental confined nematic system, with and without activity, which can be used to observe the formation and dynamics of defects in confined LCs. Through development of a model system the relationship between dynamics and length scales, such as particle or confinement size, can be systematically explored and the results of which can be directly compared to biological systems. I am developing nematic systems through specialist synthesis methods developed by the SCMB group which allow for both passive and active rod-systems. I am developing complex geometrical confinement, with the aim of probing the impact of boundary roughness, using soft lithography techniques. The combination of micron-sized rods and confinement will generate a confined nematic system which can then be imaged using high resolution confocal microscopy.

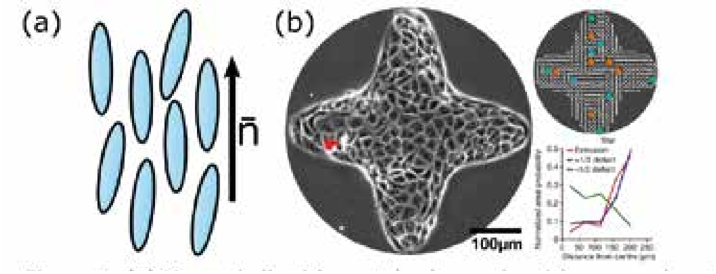

Figure 1: (a) Nematic liquid crystal schematic with arrow showing average orientation (director,n). (b) Epithelial cell extrusion is shown to correlate with +1/2 defect location[2]

[1] T. B. Saw *et al.*, *Nature*, **544**, 212-216 (2017)

Machine-learning potentials for simulations of colloidal systems

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Computer simulation, Machine learning, Colloids

Computer simulations of particle-based models are nowadays a well-established tool for studying matter. In the past few years, we have witnessed enormous advances in the development of both physically-inspired empirical and purely-mathematical potentials for simulations of atomistic models. For instance, Behler and Parrinello introduced a very elegant approach[1] to efficiently approximate the many-body interatomic potentials in atomistic systems by fitting large data sets from electronic structure calculations using artificial neural networks, thereby enabling molecular simulations with the accuracy of "first principles" calculations and the efficiency of simple atomistic "force-fields". Despite the availability of fast computers and efficient algorithms, simulations of colloidal systems consisting of mesoscopic particles with smaller species like ions or depletants remain computationally challenging as very different length and time scales are involved. Huge efforts have been devoted to speeding up simulations of these systems by employing coarse-grained (CG) models with effective interaction potentials, which are generally obtained by an ad-hoc parameterization to match specific reference data. Nevertheless, the so-obtained potentials inevitably suffer from transferability and representability issues as they do not derive from a formal integration of a selected set of degrees of freedom. In our research, we use particle-based simulations and machine learning (ML) to construct transferable CG many-body potentials for a variety of colloidal systems, including colloid-polymer mixtures and anisotropic rod-like nanoparticles. In our approach, the degrees of freedom of the microscopic species are formally integrated out and the mesoscopic particles interact with effective many-body potentials, which are then fitted as a function of all colloid coordinates with a set of symmetry functions. Our CG ML potentials lead to a reduction of computational cost by several orders of magnitude compared to simulations of the "true" systems. Hence, using these ML potentials in Monte Carlo or molecular dynamics simulations, provides us with a better understanding of the relationship between the interactions and physico-chemical properties of specific colloidal systems and enables the accurate prediction of their phase behavior. We are also interested in exploiting these efficient ML potentials for studying colloidal self-assembly pathways in bulk, droplets and drying films.

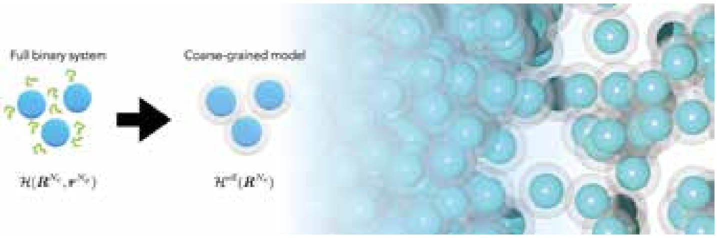

Figure 1: (Left) Schematic representation of the construction of a CG ML potential. (Right) Simulation snapshot of coexisting colloidal liquid and gas phases of a colloid-polymer mixture using a CG ML model.

[1] J. Behler and M. Parrinello, Phys. *Rev. Lett.* **98**, 146401 (2007)

Effective interactions of ligand-stabilized nanoparticles using machine learning

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Sponsor: MCEC, since March 2021
Supervisor: prof. dr. ir. Marjolein Dijkstra

Molecular simulations, Coarse-graining, Self-assembly

Colloidal nanoparticles can self-assemble into a wide variety of two-dimensional and three-dimensional superstructures with unique optical, structural and electronical properties of high interest in several fields such as optics, electronics, catalysis, biophysics and magnetic storage.[1] To control the growth of nucleation seeds and prevent aggregation in the solvent, such nanoparticles (*e.g.* gold, silica, cadmium sulfide) are stabilized by a monolayer of terminally bound organic ligands (*e.g.* amines, thiols, acids). Therefore, the type of ligand, the solvent-ligand interactions and the temperature can influence the effective interactions between the nanoparticles and ultimately their self-assembly. In order to understand the kinetic and equilibrium properties and how the effective interactions are influenced by these parameters, molecular simulations have become an invaluable tool.

In this project we perform molecular dynamics simulations using simple and computational efficient coarse-grained models of gold nanoparticles coated with alkyl chains (see Figure 1a) and polymers to measure the effective interactions between nanoparticles as a function of solvent quality, temperature, surface coverage and type of ligands. For specific size ratios between the dimension of the ligands and the nanocrystal core, the effective force between pairs of particles is largely affected by the presence of neighbor particles, therefore many-body effects are important and should not be neglected. Still, it is a common approach to build effective interaction potentials for such systems considering only up to two-body contributions. In our research, we employ a machine-learning approach to efficiently represent many-body interactions between ligand-stabilized nanocrystals (see Figure 1b) and to investigate by computer simulation, their phase and self-assembling behavior.

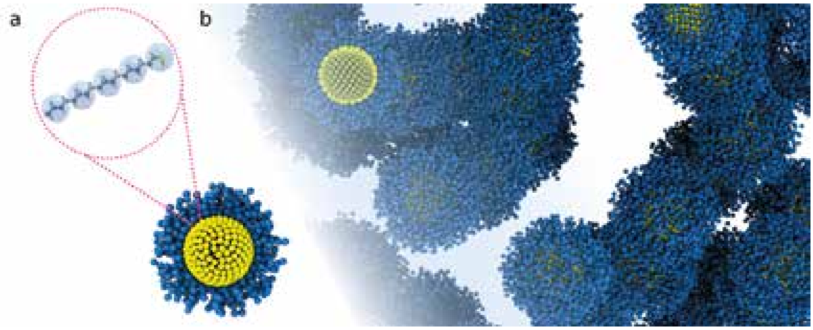

Figure 1: a) Coarse-grained model of a gold nanoparticle coated with alkyl chains. b) Simulation snapshot of a suspension of ligand-stabilized nanoparticles.

[1] P. Schapotschnikow *et al.*, *Nano letters* **8**, 2930–2934 (2008)

SERS at extreme conditions for direct catalysis evaluation

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Supervisors: prof. dr. Alfons van Blaaderen

Supraparticles, Self-assembly, SERS

Atomic vibrations and phonons are an excellent source of information on nanomaterials that we can access through a variety of methods including Raman scattering and infrared spectroscopy. In general, Raman signal are weak. Surface-enhanced Raman spectroscopy (SERS) is a methodology developed to boost the raman signal by orders of magnitude.[1] SERS can essentially be seen as a surface sensitive spectroscopic technique, as the enhancement solely take place within 10 nm of noble metal nanostructures with plasmonic properties, because at these distances the local EM fields are enhanced.

The plasmonic property of these metal nanostructures are shape and size depended. It has been reported that for anisotropic rod-shaped particles, SERS enhancements at the tips are stronger compared to spheres. Even further stronger enhancement is possible by arranging the rods standing in layers parallel with each other in so-called smectic layers with tips of nanorods close to each other.[2] Such ordered self-assembly of nanoparticles can be realized by forming supraparticles via slow-evaporation emulsion droplet method which is well established in our group.[3]

Here in this project we want to develop SERS in combination with material synthesis for high-temperature in-line monitoring of gas-phase products formed in real time. The focus of this research is to self-assemble thermally stable Au-based nanorods along with suitable colloidal nano-catalyst.[4] Ultimately, during this colloidal based self-assembly, we want the nano-catalyst to end up in between layered nanorods where the plasmonic hotspots are. Such that in these 'binary smectic' supraparticles, catalysis and SERS sensing are combined and will allow for not only following the catalytic events, but also deactivation pathways of the catalyst.[5] Major part of this project is to optimize best conditions for smectic ordering Au-based nanorods, binary self-assembly and improving SERS performance at high-temperature.

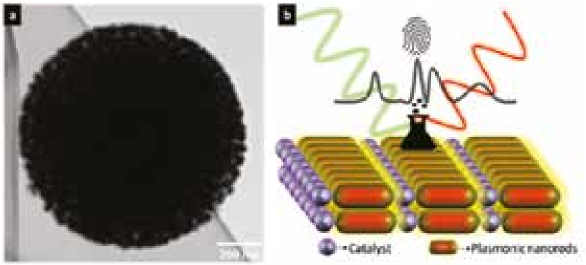

Figure 1. a) Supraparticle of non-smectic ordered mesoporous-silica coated Au nanorods b) Schematic of real time SERS during catalytic reaction

[1] H. Kim, R. P. van Duyne *et al.*, *Chem. Soc. Rev*. **39**, 4820-4844 (2010)
[2] J. Langer *et al.*, *ACS Nano* **14**, 28-117 (2020)
[3] B. de Nijs, Alfons van Blaaderen *et al.*, *Nat. Mat.* **14**, 56-60 (2014)
[4] W. Albrecht, Alfons van Blaaderen *et al.*, *Nanoscale* **9**, 2845-2851 (2017)
[5] H. E. Bakker, Alfons van Blaaderen *et al.*, *Soft Matter* **12**, 9238-9245 (2016)

Binary supraparticles: using self-assembly to control the structure in bimetallic catalysts

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Nanoparticle synthesis, Self-assembly, Electron microscopy

Self-assembly offers a promising new route in designing heterogeneous catalysts.[1] The main advantage of this self-assembly approach, with respect to conventional preparation methods, is the outstanding control over size, location and distribution of the active (metal) nanoparticles within the self-assembled catalyst, so-called supraparticle.

Supraparticles are typically tens of nanometers to a few microns sized particles composed of many nanoparticles. Crystallization of monodisperse nanoparticles into supraparticles is induced by slowly evaporating emulsion droplets containing a nanoparticle dispersion, as illustrated in Figure A. The spherical confinement induced by the shrinking emulsion droplet then results in well-defined supraparticles.

This project focusses on the synthesis of binary supraparticles, build up from two different nanoparticle building blocks. The first nanoparticle being metal based and catalytically active (for example NiPd, Fe_xO_y or $Fe_xCo_yO_z$) and the other building block serves as support material (for example Silica). Combining the two building blocks, results in a supported heterogeneous catalyst. The nanoparticles used are well controlled in shape, size and composition, see example in Figure B. In the case of bi-metallic nanoparticles, different morphologies (alloy, core-shell, separated) will be probed to compare catalytic behavior.[2] The binary crystal structure formed in the supraparticle is determined by the size ratio of the two different nanoparticle building blocks used.

Nanoparticles and supraparticles are analyzed using electron microscopy techniques. TEM tomography can be used to resolve the 3D structure of binary supraparticles.[3] Eventually the binary supraparticle serves as an extremely well-defined model catalyst particle and will be used in catalytic test.

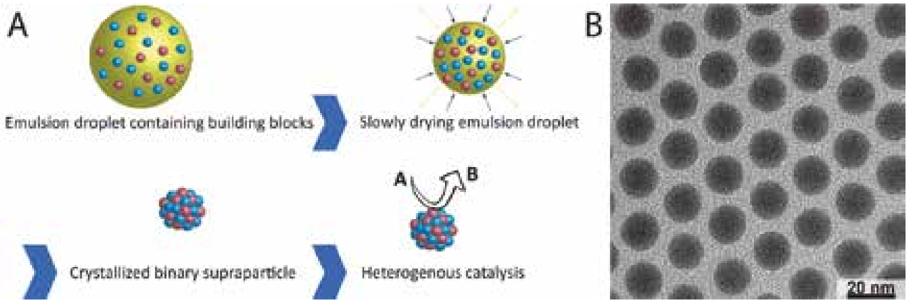

Figure: A) Schematic illustration of the self-assembly of nanoparticles into binary supraparticles. B) TEM image of stoichiometric NiPd nanoparticles. Particles have a core diameter of 10.5 nm with less than 4% size polydispersity.

[1] Y. Kang *et al.*, *JACS*, **135**, 1499-1505 (2013)
[2] J.E.S vd Hoeven *et al.*, *Nat. Mater.*, **20**, 1216-1220 (2021)
[3] D. Wang *et al.*, *Nat. Commun.*, **9**, 2228 (2018)

Crystal nucleation of complex colloidal suspensions

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Supervisors: dr. Laura Filion, prof. dr. Marjolein Dijkstra
Colloids, Computer simulations, Crystal nucleation

When you supercool a fluid, it crystalizes, i.e. the particles which are disordered in the fluid spontaneously rearrange themselves into an ordered crystal structure. It seems like a straightforward process; however, there are many questions regarding crystal nucleation over which scientist have puzzled for years, and still have not found the answers to. We try to shed some light on one of these questions: can we predict which crystal structure forms from a given fluid?

To answer this question, we focus on the fluid by trying to find hidden local motifs in this globally disordered phase that predate the birth of a crystal nucleus, see Figure 1. In recent years, various methods for identifying local structure have been developed, of which one of the most commonly used method is local bond-order parameters (BOPs) [1], which characterize local symmetries using spherical harmonics. However, when searching for small signals of (unknown) local structure in the fluid, it is important not to let your expectations and method bias your findings. That is why we combine different methods, such as BOPs, topological cluster classification [2], and unsupervised machine learning [3], to search for local structural differences in the fluid of various colloidal model systems, both of isotropic and anisotropic particles, which might predict crystal nucleation.

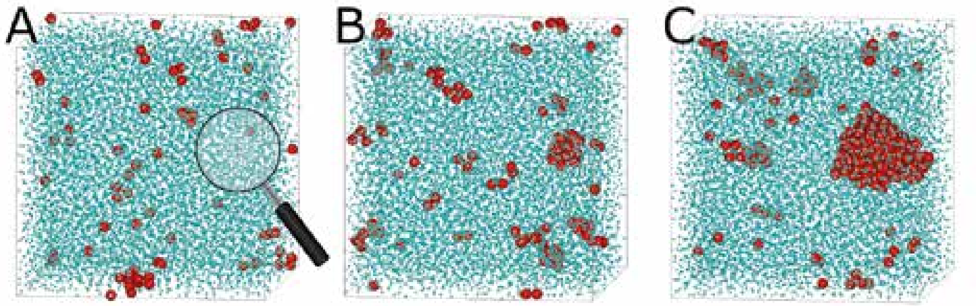

Figure 1: A typical crystal nucleation event, with A) a snapshot of the system before nucleation started, B) just after the birth of a crystal nucleus, and C) well into the crystallization process. Particles classified as crystal are colored red, and particles classified as fluid are colored blue and displayed at a quarter of their actual size to make the crystal nucleus visible. The magnifying glass in A) represents our focus on the region of the fluid where the crystal nucleus is born.

[1] W. Lechner *et al.*, *J. Chem. Phys.* **129**, 114707 (2008)
[2] A. Malins *et al.*, *J. Chem. Phys.* **139**, 234506 (2013)
[3] E. Boattini *et al.*, *J. Chem. Phys.* **151**, 154901 (2019)

Nanosensors for local halide concentrations

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Supervisors: dr. Freddy T. Rabouw, prof. dr. ir. Bert M. Weckhuysen and prof. dr. Alfons van Blaaderen

Fluorescence microscopy, Quantum dots, Lanthanide-doped nanocrystals

Most common catalyst particles are host to a complex network of pores and a substantial fraction of actives sites may be embedded deep within. Transport of reactants into the pore structure and subsequent outward diffusion of products is not always straightforward (for instance, it depends on the size and shape of the pores and the molecular species). In order to rationally design future catalyst structures, it is crucial to get a better understanding of molecular transport in porous systems. In this work, we introduce a novel method to visualize the diffusion front of halide species based on luminescent perovskite nanocrystals that change color when exposed to halide ions in their local environment. The concept of tracking halide diffusion serves as a general model system that will help to improve future catalyst design.

Perovskite nanocrystals

In recent years, nanocrystals of cesium lead halide perovskites ($CsPbX_3$; X = Cl, Br, or I) have drawn a lot of attention thanks to their unique optoelectronic properties.[1] The optical properties can be effectively tailored by controlling the type of halide ions incorporated into the nanocrystals. Specifically, it is possible to tune the color of photoluminescence across the entire visible spectrum by varying the halide composition—with $CsPbCl_3$ $CsPbBr_3$ and $CsPbI_3$ emitting blue, green and red, respectively.[2] Interestingly, when foreign halide species are introduced in the medium surrounding the perovskite NCs, native halide ions can be replaced in a process called anion-exchange.[3] Since the exchange reaction induces changes in the halide composition, the optoelectronic properties change accordingly. As such, when incorporated inside a pore structure, $CsPbX_3$ NCs are promising candidates as nanosensors to track the diffusion front of halide ions by means of in-situ optical micro-spectroscopy.

[1] Q.A. Akkerman *et al. Nat. Mater.* **17**, 394–405 (2018).
[2] L. Protesescu *et al. Nano Lett.* **15**, 3692–3696 (2015).
[3] G. Nedelcu *et al. Nano Lett.* **15**, 5635–5640 (2015).

High resolution 3D structural analysis of hydrotreating catalysts using electron microscopy

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Sponsor: ARC-CBBC, since 1st September 2021
Supervisors: prof. dr. Alfons van Blaaderen, dr. Marijn van Huis (UU),
dr. Jovana Zečević (Shell)

Supported metal catalysts, High-resolution 3D-TEM

The performance of heterogeneous catalysts is known to be strongly dependent on a complex interplay between various structural features of the catalysts at multiple length-scales. From the macroscale porosity of shaped catalysts defining the accessibility of feedstock molecules and removal of products, down to metal (oxide, sulphide) catalyst nanoparticles and their atomic (im) perfections governing the catalytic reactions. To be able to control the structure and ultimately tune the catalyst performance, it is essential that the impact of catalyst synthesis conditions on structure is understood. Hydrotreating catalysts are an example of heterogeneous catalysts with an exceptionally complex structure on multiple length scales.[1] They are composed of a mixed-metal (Ni/Mo, Co/Mo, Ni/W, Co/W) sulphide phase, supported on a porous oxide support (usually alumina).

In this work we study NiMoS slabs, the interaction of these slabs with the support surface, the relative position of the Ni and Mo atoms, and ultimately how the obtained structure influences their activity and selectivity. We aim to resolve the catalyst structures in 3D at (near) atomic scale by using electron tomography (ET) and by developing novel imaging methods using a segmented-detector, direct electron detection camera and varying beam voltages, as well as methodology allowing combining the characterization with EELS and EDX elemental imaging. To date there are only a few examples where (Ni)MoS catalysts were imaged in 3D. [2, 3, 4] The resolution was however limited and did not allow a detailed analysis of individual (Ni)MoS slabs, but it provided insights into features such as (presumably) MoS_2 slabs confined in alumina pores. With the new advances in electron microscopy, we want to push the boundaries and arrive at unprecedented 3D (elemental) resolutions of NiMoS slabs in industrial catalysts and discern the effect of the different structures on catalyst performance.

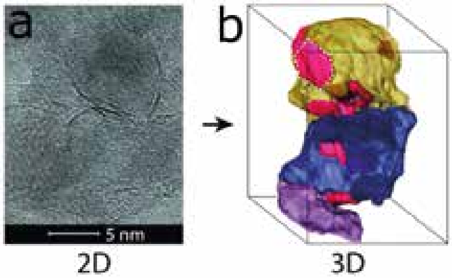
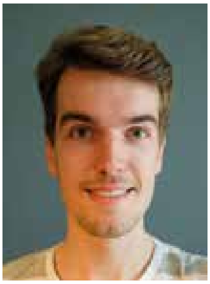


Figure 1: a) TEM micrograph of MoS_2 supported on titania-alumina and the b) tomographic reconstruction. Figure reproduced from reference [4].

[1] R. Prins et al., vol. 4, Wiley-VCH, Weinheim, p.1908 (1997)
[2] K. P. de Jong *et al.*, *J. Phys. Chem. B* **110**, 10209-10212 (2006)
[3] M. Ramos *et al.*, *Scientific Reports* **7**, 12322(1-9) (2017)
[4] S. Eijbouts *et al.*, *ACS Catalysis* **7**, 4817-4821 (2017)

Multiscale structuring by microfluidics and self-assembly of nanoparticles for heterogeneous catalysis and sensing



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Supervisors: prof. dr. Alfons van Blaaderen, prof. dr. ir. Mathieu Odijk (University of Twente)

Microfluidics , Self-assembly, Nanoparticles

Current techniques for making monodisperse droplets are either optimised for production of small, (sub)micron droplets or high throughput.[1-2] Monodisperse micron-sized droplets pose interesting applications in the field of colloid science, as model systems, as well as in many other fields such as catalysis and sensing, as they prove to be a great tool in self-assembly of nanoparticles into organised structures (supraparticles, SPs).[3-5] In this project, we aim to improve current parallelised step-emulsification systems by downscaling and increased parallelisation, in order to generate micron-sized droplets with high yield, potentially at gram-scale.

Drying droplets of dispersions of nanoparticles has proven to be a versatile method to generate ordered SPs. [3-5] Using this process, we have control over size of the nanoparticles, size of the supraparticles (by controlling the droplet size) and size of the suprastructures (by controlling the amount of supraparticles).

In our microfluidics chip, developed by collaborators at the University of Twente, droplets emerge from a shallow channel into a deep cavity containing the
continuous phase, as depicted in Figure. 1b. Droplet size only depends on device geometry and properties and is independent of used flow speeds.[1]

Analysis of the droplets is carried out using (confocal) fluorescence microscopy – by incorporation of a fluorescent dye inside the droplets – and static light scattering measurements. The formed supraparticles are analysed using transmission and scanning electron microscopy techniques.

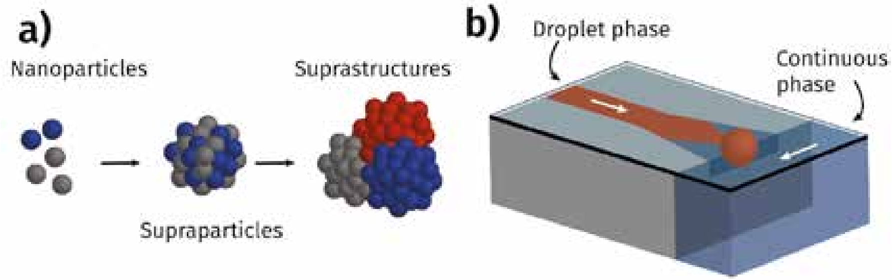

Figure 1: a) Overview of structuring at multiple length scales. b) Schematic view of one nozzle of our microfluidics chip.

[1] E. Amstad *et al.*, *Lab Chip* 16, 4163–4172 (2016)
[2] Y.Y.P. Sang *et al.*, *R. RSC Adv.* 3, 2330–2335 (2013)
[3] S. Park *et al.*, *Nanoscale* 12, 18576–18594 (2020)
[4] D. Wang *et al.*, *Nat. Phys.* 17, 128–134 (2021)
[5] M. Schwarze *et al.*, *Sci. Technol.* 5, 24–33 (2015)

Optical control over the blinking behavior of colloidal quantum dots

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Supervisors: dr. Freddy Rabouw, prof. dr. Alfons van Blaaderen
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Single-particle spectroscopy, Quantum dots

Colloidal quantum dots are very small semiconductor nanocrystals that show fluorescence of bright colors tunable across the visible part of the electromagnetic spectrum by the size of the nanocrystal (Fig. 1a; increasing size of CdSe nanocrystals from left to right). Although all vials appear very bright under ultraviolet illumination, zooming in would show particle-to-particle variations of the emission intensity (Fig. 1b). Interestingly, even on the single-particle scale the emission intensity fluctuates seemingly random in time between a high-intensity ON level and a low-intensity OFF level (Fig. 1c). This peculiar phenomenon is called blinking and has been observed in nearly all types of semiconductor nanocrystals, *e.g.* CdSe, InP, CuInS2, $CsPbBr_3$.[1] Blinking is unwanted for many applications like lighting and television displays where bright emission is important. On the other hand, in super-resolution microscopy, blinking is used to disentangle the emission from multiple single emitters from overlapping diffraction limited spots.

In my project, we investigate the physical origin of blinking with the goal to eventually control its behavior to match the application at hand. Recently, it has been suggested that blinking is related to temporal storage of excitations in nanocrystals by imperfections in the crystal and/or on the surface. [2] Release of the excitation by optical pulses could prevent switches from the ON to the OFF state and could serve as a tuning knob to control blinking.

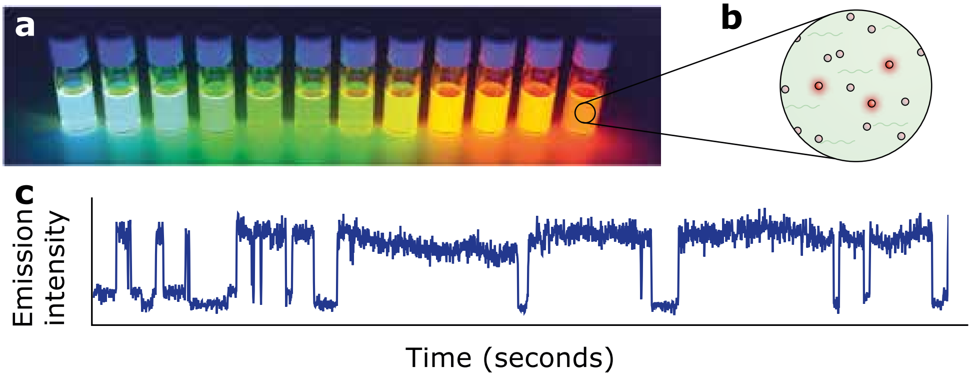
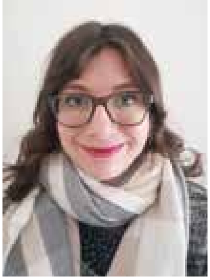


Figure 1: a) Semiconductor quantum dots of different sizes (increasing size from left to right) showing different emission colors under constant illumination. b) Schematic zoom-in showing particle-to-particle variations of the emission intensity of colloidally stable quantum dots in an organic solvent. c) Typical emission intensity over time shows chaotic blinking between high and low emission.

[1] Nirmal *et al.*, *Nature* **383**, 802–804 (1996)

[2] Rabouw *et al.*, *Nano Lett.* **15**, 7718–7725 (2015)

Effect of many-body interactions on the structure and phase behavior of microgel particles



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Molecular simulations, Many-body interactions, Microgel particles

A quite versatile type of particles that we can find in colloid science are microgel particles. These particles respond by changing their size, to different external stimuli such as a change in temperature or pH. This characteristic makes them interesting as they could change their phase behavior as a function of temperature, passing from a hard-sphere-like to a soft-sphere like behavior. However, one of the main challenges is to accurately model them through molecular simulations, as their interaction potential can change as a function of temperature.

One way of modelling them is through soft repulsive potentials, such as the Hertzian potential. These types of potentials present a rich phase diagram at low temperatures. [1] However, these phases have not been seen in experiments. One of the possible reasons is that the interaction is pairwise and at the regime of high densities and low temperatures, where crystallization or the glass transition are expected, there are multiple overlaps between the particles, and they tend to either facet or deform.[2] Hence, in this regime we expect many-body interactions to play an important role. See Fig. 1a.

Here, I will explore the effect of many-body interactions on the phase diagram of colloidal particles interacting with a soft repulsive potential. To do so, I use a simple model of a microgel coated particle. The soft shell of the particle is discretized and with this we capture the elastic deformations of the microgel shell due to the presence of neighboring particles as in Ref.[3] This type of interactions tends to be computationally expensive and to overcome this problem we use a machine-learning potential where the many-body interaction is fitted as a function of the colloid coordinates with a combination of symmetric functions.

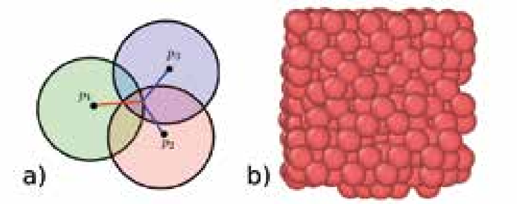

Figure 1 a) Scheme of a three-body interaction, where in the central part the tree particles are interacting. b) A typical crystal found in the many-body model simulations.

I explore through molecular simulations the phase diagram of microgel particles interacting with a pairwise potential and with the many-body interactions at different temperatures and pressures. To compare the differences between the two models, we use free-energy calculations of the different crystals that we find in the phase diagram (see Fig. 1b).

[1] J. Pàmies *et al.* *J.Chem. Phys.* **131**, 044514 (2009)
[2] A. Scotti *et al.*, *J. Chem. Phys.* **148**, 17 (2018)
[3] E. Boattini *et al.*, *J. Chem. Phys.* **153**, 064902 (2020)

Homogeneous crystal nucleation of colloidal systems

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Crystallization, Polymorph selection, Nucleation mechanisms

Studying the formation of colloidal crystals may facilitate their synthesis, as well as advance our general understanding of self-assembly and phase transitions. I study crystallization through simulations of homogeneous nucleation, i.e. away from surfaces or impurities.

Given a fluid with known interactions (*e.g.* a screened Coulomb interaction for charged colloids), I am firstly interested in predicting the rate of nucleation and the crystal structure that will form first (polymorph selection). For this, I employ the seeding technique[1], which relies on classical nucleation theory and molecular dynamics.

Since it can take a large amount of (computer) time for a crystal nucleus to form in a fluid, I use both rare-event techniques and brute force methods to simulate that process. Next, I describe the structural changes that happen during nucleation with the topological cluster classification algorithm[2] and with bond order parameters. This yields insight into the actual mechanism of nucleation.

Currently, I am investigating nucleation of Lennard-Jones particles, colloid-polymer mixtures (Asakura-Oosawa) and charge-stabilized colloids (Yukawa). In the future, this may be extended to nucleation with machine-learning potentials and inverse design.

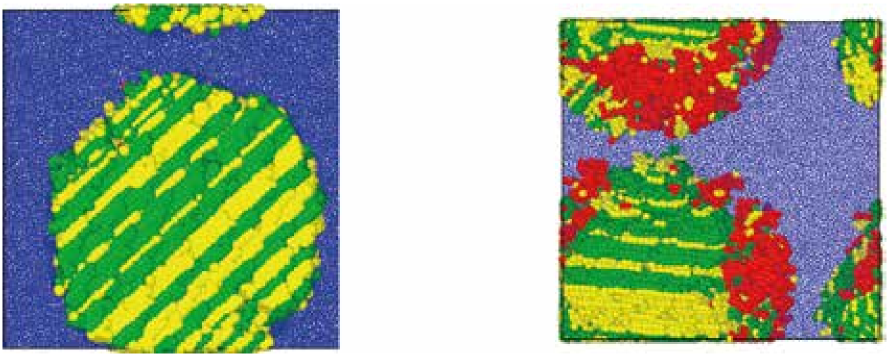
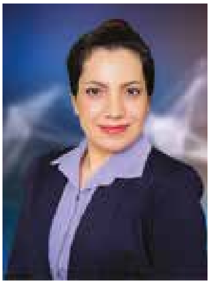


Figure 1: (left) Crystallization of Lennard-Jones particles with random stacking of face-centered cubic (fcc, yellow) and hexagonal close-packed (hcp, green). (right) Crystallization of hard-core Yukawa particles with fcc, hcp and body-centered cubic (bcc, red).

[1] J.R. Espinosa *et al.*, *J. Chem. Phys.* **144**, 034501 (2016)
[2] A. Malins *et al.*, *J. Chem. Phys.* **139**, 234506 (2013)

Towards structuring silica and titania based supraparticles



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Supervisors: Prof. dr. Alfons van Blaaderen, Dr. Arnout Imhof

Photonic crystals, Supraparticles, Rattler particles

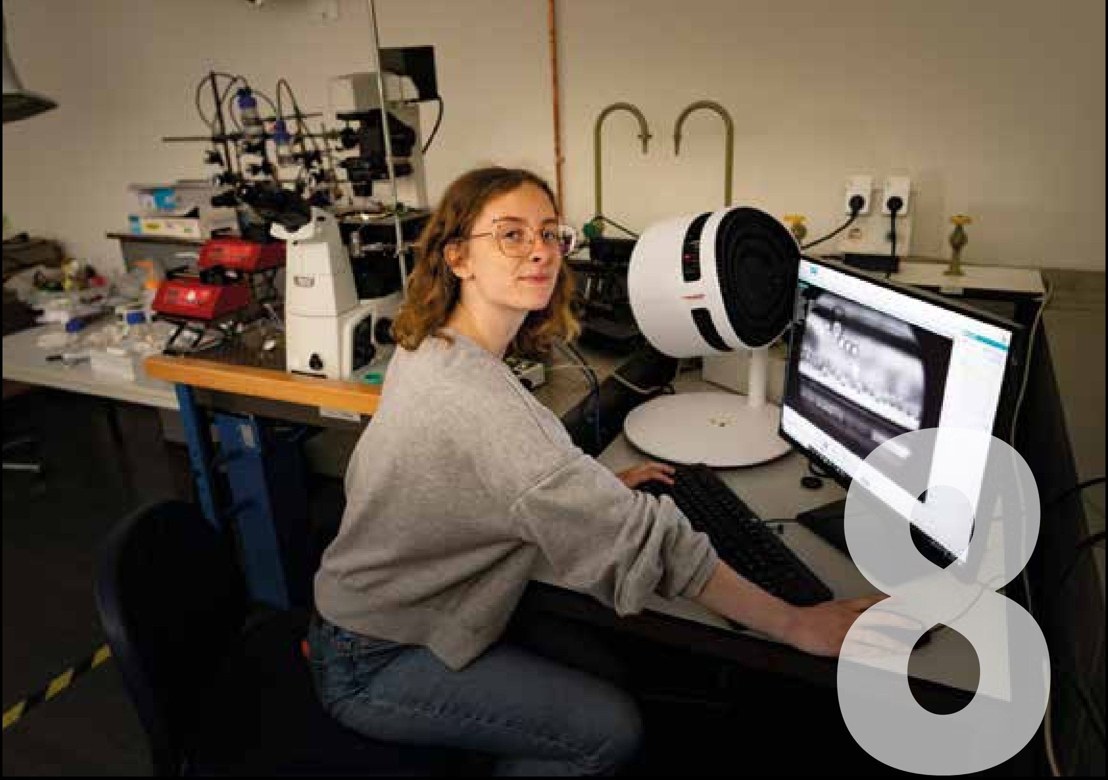
Photonic crystals (PCs) made of titania attract great attention owing to perspectives for practical applications in optoelectronics, sensing, and photovoltaics.[1] A photonic crystal (PC) is a regularly structured material, with feature sizes on the order of a wavelength (or smaller), that exhibits strong interactions with light.[2] Due to the fairly large refractive index (~2.5 of anatase, and ~2.7 of rutile), which is large enough to form a photonic band gap in PC structures and lack of absorption of visible light, TiO_2 is especially attractive.[3] One of the approaches to the fabrication of photonic crystals is self-assembly of colloids which is simple, fast, and cheap. Due to their size and ability to self-organize into 3D periodic structures with different symmetries, colloidal particles are ideal building blocks for the creation of photonic crystals[4] we present experimental work on the characterization of photonic colloidal crystals in real and reciprocal space. Photonic crystals are structures in which the refractive index varies periodically in space on the length scale of the wavelength of light. Self-assembly of colloidal particles is a promising route towards three-dimensional (3-D).

In this project, the prepared titania-silica core-shell particles sterically stabilized by grafting with short C_{18} alkane chains, will be self-assembled in both bulk crystals and if successful also in emulsion oil droplets for more close packed supraparticles. For the photonic crystals made of titania and silica, silica spheres should be made in the same size as titania particles, then the close packed and long ranged crystal structures could be made by using a mixture of these two components.

We also investigating making dispersion supraparticles. The usual supraparticles are dried but here we intend to make a solid silica shell around the dispersion of particles. For this purpose, the oil droplets containing nanoparticles will be coated by silica.[5]

Another project is a collaboration with Kanako Watanabe who is visiting SCM from Sendai University (Japan). We are investigating dye diffusion inside refractive index matched hollow shells in silica rattler particles, which consist of a core particle which can move in a void enclosed by a shell [6]*"ISSN":"15205002","abstract*":"We present the synthesis of new shapes of colloidal silica particles by manipulating their chemical composition and subsequent etching. Segments of silica rods, prepared by the ammonia catalyzed hydrolysis and condensation of tetraethylorthosilicate (TEOS). The analysis of dye diffusion inside the shells, can be measured directly by analyzing the fluorescence inside the shells or indirectly from core movements using confocal microscopy. At a later date, the same measurements can be done with titania rattles for comparison, which are more interesting for applications but harder to image quantitatively.

[1] N. A. Sapoletova et al., *Electrochem. commun* **91**, no. April, 5–9 (2018).
[2] *K.P. Velikov*, Towards a complete photonic band gap in the visible., 2002.
[3] X. Wang et al., *Opt. Express* **13**, 1486 (2005).
[4] J. H. Thijssen, *Characterization of photonic colloidal crystals in real and reciprocal space*, 2007.
[5] P. Xu *et al., Mater. Lett* **205**, 20–23 (2017).
[6] F. Hagemans *et al., Chem. Mater* **29**, 3304–3313 (2017).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VAN ‘T HOFF LABORATORY FOR PHYSICAL AND COLLOID CHEMISTRY

Scientific staff	prof. dr. Albert Philipse, prof. dr. Willem Kegel, dr. Ben Erné, dr. Andrei Petukhov, dr. Martin F. Haase,
Adjunct staff	prof. dr. Henk Lekkerkerker, prof. dr. Jan Groenewold, dr. Hans Tromp
Technical support	drs. Bonny Kuipers, dr. Alex van Silfhout, dr. Dominique Thies-Weesie
Administrative staff	Sylvia Visser
PhD students/Postdocs	13

Research Mission

In the Van ‘t Hoff laboratory for Physical and Colloid Chemistry at Utrecht University the focus of our teaching and research is on the physical chemistry of objects with sizes between several nanometers and micrometers, the so-called ‘colloidal scale’. Understanding the behavior of matter at the colloidal scale, being in between the sizes of (simple) molecules and macroscopic objects, is important for many scientific disciplines including biology, geosciences, physics, and engineering.

In our group we work on a broad range of topics. We create new model systems, perform experiments with state-of-the-art techniques, and develop new theory. There are ongoing national and international collaborations with academic groups as well as with industry. Knowledge of the interactions and structure formation of matter at the colloidal scale has facilitated important technologies such as electronic displays, microprocessors, and artificial drug and gene delivery vehicles.

Examples of our current research lines are:
- *Structure formation and dynamics in well-defined colloidal dispersions in bulk and at interfaces;*
- *Porous systems for nanofiltration, catalysis, and electrochemistry;*
- *Self-assembly of viruses and virus-like objects;*
- *Self-propelling colloids;*
- *Magnetic fluids and their use in plastic waste separation;*
- *Colloidal crystals with applications as photonic materials;*
- *Thermodynamics of charged colloids and interfaces;*
- *Model systems for genetic regulation*

Electro-osmosis and biphasic catalysis in bijels

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Supervisors: dr. Martin F. Haase

Bicontinuous emulsions, Electrokinetics, Biphasic catalysis

Chemical reactions involving 2 immiscible liquid reactants and solid catalyst particles are limited in their reactivity because the catalytic sites are typically not accessible to both reactants. However, by locating the catalyst particles at the interface of two immiscible reactants, all three participants meet and the reaction can proceed swiftly. Based on this concept, we employ colloidal particles at interfaces to structure liquids into a long network composed of microscopic channels, a material known as a bijel fiber. (fig. 1A) The large surface area of a bijel enhances the reactivity because it facilitates intimate contact between reactants and catalysts. Moreover, the two interwoven channel networks of oil and water allows reactants to flow in, and products to be continuously withdrawn. This approach shows promises to introduce a new chemical technology for the synthesis of high value-added chemicals. However, before industrial implementation can be realized, several research questions still need to be investigated.

Research is now focused on three main topics, all working towards continuous biphasic catalysis. Firstly, learning how to better control the bijel formation process. Currently, silica particles are placed on the interface, to realize catalysis in a bijel, bijels containing catalytic particles are required. Secondly, we investigate the flow of liquids through the bijel fiber. A convective flow is required to sustain a catalytic reaction. Pressure driven flow is impractical through the long submicron water pore network, so we make use of electro-osmotic flow. (fig. 1B) With the help of confocal microscopy, we investigate the behavior of the liquid flow through the complex material on micron scale. Lastly, the synthesis of dyes inside the bijel is used to learn about its catalytic activity and limitations. (fig. 1C) The reaction rates will provide us insight on how the unique system can be employed in an industrial setting.

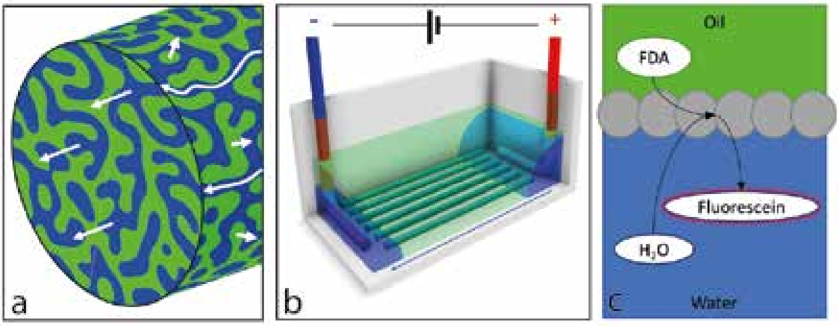

Figure 1: a) Schematic of the bijel fiber, with water (blue) and Oil (green) networks intertwined. b) Schematic of parallel fiber electro-osmosis setup. c) Catalytic conversion of Fluorescein diacetate to fluorescein.

To the next level of transcription: the influence of the accessible genome size

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Supervisors: prof. dr. Willem Kegel, dr. Gert Folkers

Transcription regulation, Thermodynamic models, RNA polymerase

Transcription is the process in which RNA polymerase synthesizes messenger RNA during the readout of a gene segment on the DNA. This process is regulated by, amongst others, transcription factors. These are proteins that activate or repress transcription by binding to specific locations on the DNA, such as near the promoter of a specific gene, which is the binding location of RNA polymerase. However, these proteins also bind to other parts of the DNA and thus, the total amount of DNA available for these proteins to bind to competes with the specific binding to promoter regions.[1]

Somewhat surprisingly, this 'next level' of transcription regulation has not been systematically addressed yet. Indeed, several processes in the cell are expected to lead to significant variations in the amount of accessible DNA to the proteins involved in transcription regulation. This affects the chemical potential of the proteins involved, which in turn influences the fraction of bound proteins to the promoter and operator regions, and thus the overall transcription rates. Such behavior follows from the basic statistical thermodynamics for simple genetic architectures.[2]

In this project we quantitatively investigate how non-specific DNA influences transcription, and expand the theoretical framework that predicts transcriptional behavior. To determine the effect of the number of non-specific base-pairs on the transcription rate, transcription rates will be monitored using a Lac operator in a simple repression architecture. A construct called Broccoli-DNA[3] is used as a reporter gene, which is transcribed into mRNA aptamers that fluoresce upon binding to an appropriate chromophore (DFHBI-1T). This allows us to directly measure transcription in vitro in real time.

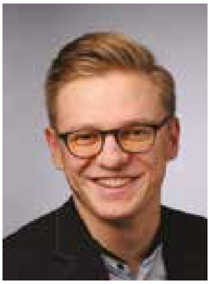
If successful, this work will pin down the regulatory role of the accessible genome size in biological cells and provides a next level of transcription regulation, that is, regulation beyond the direct interactions between operator regions and transcription factors.

[1] Franz M. Weinert *et al.*, *Phys. Rev. Lett.* **113**, 258101 (2014).

[2] J. Landman *et al.*, *Phys. Rev. Research* **1**, 033094 (2019).

[3] J. Ouellet, *Front. Chem.* **28** (2016).

Desalination in high-surface area membranes templated by bicontinuous interfacially jammed emulsion gels



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Sponsor:	NWO, since March 2021
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Bijel, Confocal microscopy, Desalination

Bijels (bicontinuous interfacially jammed emulsion gels) are formed by arresting the spinodal decomposition of two immiscible liquids with surface active nanoparticles. This results in an interwoven fluid network separated by a percolating film of nanoparticles. The percolating nanoparticle film provides the bijel with a large internal surface area and a distinct pore network with pore sizes ranging from 100 nm to 5 µm. On this internal surface, a semipermeable membrane will be synthesized to facilitate reverse osmosis and/or nanofiltration.

To separate hydrated salt ions or dissolved organic molecules, the pores of the bijel are connected to both feed and concentrate flow side of the membrane. A key challenge in membrane application is overcoming concentration polarization in the bijel network due to salt accumulation. Thus, engineering and implementing a tailored drainage structure into the membrane will be investigated in the project.

The performance of the high-surface area membrane is evaluated by measuring the permeate flux, as well as the solute concentrations in permeate and concentrate streams. Confocal laser scanning microscopy is employed to spatially visualize the concentration profiles of solutes within the membrane by using fluorescent tracer molecules.

Self-assembly of building blocks with conformational switches

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Copolymers, Polymer synthesis, Self-assembly

The chemical, architectural, and size versatility of copolymers makes them ideal molecules to probe fundamental self-assembly concepts. The main aim of the project is to design and characterise polymers that exhibit conformational switches. These may be triggered by external factors such as pH or be implicit to the molecular architecture.

One family of pH sensitive polymers are hydrophobic polyelectrolytes (HPEs), which contain both ionizable and hydrophobic groups. They present sharp pH-induced conformation (see figure) and solubility transitions due to the competition between their amphiphilic components.[1]

These transitions can be compared to statistical mechanical models to gain a better insight into the origin of sharp transitions, which are very prevalent in biological processes. An example of such a polymer is poly(butyl-acrylate)-statistical-poly(acrylic acid) which can be synthesized with a very low polydispersity using radical polymerization techniques. HPEs show great promise for chemical and biological sensing[2], for targeted drug delivery into tissues with pH gradients, such as cancerous tissue [3], and they are extensively used in the solubilization of cell membranes allowing for the characterization of proteins in their native environment. [4] Polymer architecture plays an important role in polymer conformation, surface adsorption and membrane solubilization ability, therefore this is an area of research in the project too.

By combining a hydrophobic polyelectrolyte block with other blocks to create a diblock or multiblock copolymer cargo-delivery nanoparticles can be designed. The use of HPEs may allow for drug release at very specific pHs and within very small pH ranges.

The phenomena behind the formation of copolymer assemblies can be very complex. This project also aims to look at the possible hysteresis that may be present in systems which contain conformational switches. It has been proposed that the anomalous stability of viral capsids relies on a similar mechanism.[5]

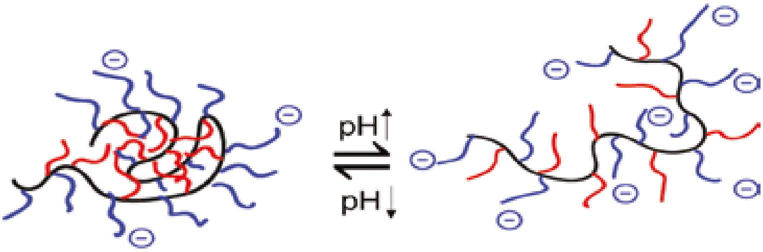

Figure 1: Schematic of a pH-driven coil to globule transition.

[1] M.A. Yessine *et al.*, *Adv. Drug Deliv. Rev.* **56**(7), 9991021 (2004)

[2] Y. Li, T. Zhao *et al.*, *Nat. Commun.* **7**(1), 1–11 (2016)

[3] F. Reyes-Ortega, Smart Polymers and their Applications, Chapter 3, 45–92, *Woodhead Publishing* (2014)

[4] J.M. Dörr *et al.*, *Eur. Biophys. J.* **45**, 3-21 (2016)

[5] G.R. Lazaro *et al.*, *J. Phys. Chem. B* **120**(26), 6306–6318 (2016)

Experimental thermodynamics of ion confinement in porous carbon electrodes

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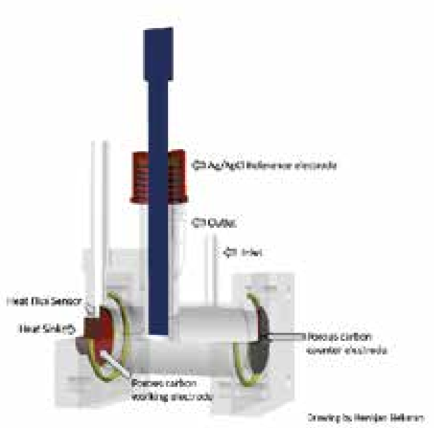
Electrochemistry, Thermodynamics, Experimental

Shortage of drinking water affects around 15% of the people worldwide. One possible solution for this problem is desalination of brackish water by adsorbing the salt in porous carbon electrodes. Porous carbon electrodes in use for this application consist of mesopores with rapid ionic transport, and micropores, the latter having a width of around 3-4 times the size of a water molecule. These pores lead to a very high specific surface area of around 1400 m^2/g of porous carbon.

Electric double layers form in the electrodes, as a result from interactions of ions in solution with each other and with the charged surface of the charged electrode surface. The formation of these double layers leads to a decrease in the configurational entropy of the ions, which can be measured as a heat effect. The thermodynamics of the double layers is a subject of present day experimental and theoretical research, and many questions still remain to be answered. For instance, how the thermodynamic properties of these double layers depend on the ion size and valency and the pore size. The goal of our research is to contribute new fundamental insight into how the volume of ions limits the high capacity of the porous carbon electrodes to adsorb aqueous salt.

During the course of this project we have realized a setup based on a Heat Flux Sensor. Using this setup (shown in Figure 1) we have measured the reversible heat of the charging and discharging of the electrical double layer in different salt solutions on a single porous carbon electrode. Furthermore, we are using NMR to get insight in the distribution of the ions in the pores of the porous carbon.



Drawing by [illegible]

Figure 1: The electrochemical cell based on a Heat Flux Sensor

Interfacial polymerisation within a bijel

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Bicontinuous emulsions, Interfacial polymerisation

Bicontinuous interfacially jammed emulsion gels (bijels) are soft materials with two interpenetrating continuous liquid domains stabilised by colloidal particles (see Figure 1). Due to the large surface area of the interface compared to the volume and the possibility of two continuous liquid domains, the bijel lends itself to many possible applications. The bijel, as it is composed of two liquid domains, can be easily broken and is unable to withstand the high pressures necessary for many of these applications. One way to improve the mechanical integrity is to reinforce the colloidal silica particles at the interface. To this end, we employ interfacial polymerisation. This has the additional benefit of providing a selective membrane at the bijel interface that could be used for desalination or other separation processes.

How do we make a bijel?

The bicontinuous structure of the bijel can be reliably formed by the interfacial jamming of particles during the phase separation of immiscible liquids via spinodal decomposition. We use the method of solvent transfer induced phase separation (STrIPS) to continuously produce bijel fibres where the removal of the solvent from a ternary mixture results in phase separation (see Figure 1). [1]

What is interfacial polymerisation?

Interfacial polymerisation describes a polymerisation reaction that occurs across an interface and is confined to that interface because one of the necessary reagents is only soluble in one of the liquid phases and another necessary reagent is only soluble in the other liquid phase. These reagents can then only come into contact at the interface between the two phases. The resulting polymer film is then limited in thickness because the components cannot easily diffuse through the formed film.

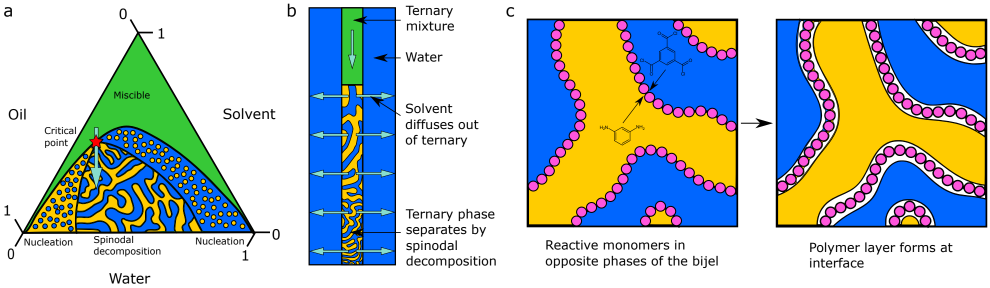

Figure 1: a) A diagram showing the phase separation of a ternary mixture that occurs with solvent removal. b) A diagram showing the process of bijel fibre formation by the STrIPS method. c) A diagram showing the process of interfacial polymerisation occurring in the bijel.

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Bijel-templated membranes for nanofiltration and desalination

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Bijels, Membrane separation, Transport phenomena

As water scarcity poses a growing threat to several parts of the world, there is a pressing need to increase our water supply through purification of unconventional water resources such as seawater.[1] A common membrane-based technique to purify seawater for everyday use is desalination. The pore size of these membranes is such that water molecules can pass the membrane, but hydrated salt ions and other solutes are rejected.

However, current membrane-based technologies are fundamentally limited in their throughput. Separations requiring high selectivity, such as desalination, are characterized by low permeabilities. This project aims to employ bijels as templates for high specific surface area membranes in order to increase the membrane permeate flowrates up to two orders of magnitude.

Bicontinuous interfacially jammed emulsion gels (bijels) can be prepared using a technique called solvent transfer-induced phase separation (STrIPS).[2] In STrIPS, a mixture of water, oil and solvent undergoes spinodal demixing upon solvent removal. In this demixing process, an interpenetrating network of oil and water channels is formed. Coarsening of the network is arrested by adsorption of nanoparticles onto the fluid-fluid interface. The obtained bijels have large internal surface areas up to 10 m^2/cm^3.

This project investigates molecular separations within bijels based on multiple steps. First of all, the architecture and mechanical properties of bijels will be tailored to overcome diffusion limited transport in the membrane. An approach will be sought to connect the channels of the bijels to their respective bulk phases without particle aggregation blocking the way. Afterwards, ultrathin selective polymer layers can be generated within the bijels by interfacial polymerization. Finally, the interplay of convection, diffusion and permeation will be quantified based on a combination of confocal laser scanning microscopy and modelling. The results from this project will enhance our understanding of fluid transport in porous materials and introduce a technology to overcome limitations of state-of-the-art membranes.

[1] J.B. Werber *et al.*, *Environ. Sci. Technol. Lett.* **3**, 112-120 (2016)
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Interfacial catalysis within bijels: a sophisticated route to saving energy?

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Bijels, Interfacial catalysis, Microfluidic devices

In 2005 a new class of soft-materials consisting of two interpenetrating, continuous networks of immiscible liquids was introduced. [1] These rigid structures are known as bicontinuous interfacially jammed emulsion gels (bijels) which are stabilized by a jammed layer of colloidal nanoparticles (NPs). Their high surface-area porous channel network, containing both an oil- and water phase and the presence of NPs lead to potential applications in various areas like catalysis, separation mediums and sensors.[1]–[4]

In this project, we will investigate the catalytic application of bijels as new type of industrial reactor. Nowadays, the syntheses of chemicals and pharmaceuticals consume large amounts of energy, leave toxic solvent waste behind and utilize over 15% of the global energy consumption to purify the products. [5], [6] Bijels can reduce this expenditure since the reaction and separation occur simultaneously within one single step. Due to the different liquid polarities, both the reactants and products can partition into one of the phases (figure 1). Furthermore, bijels can facilitate close contact between immiscible reagents. This renders the use of organic solvent superfluous, making catalytic bijels economically feasible too.[7], [8]

The main objectives of this project are to prepare, characterize and test catalytically active bijels. Different NPs which can both stabilize the immiscible liquids and are catalytically active will be tested. Preparation will be executed by the valuable method of solvent transfer induced phase separation (STrIPS) using microfluidic devices to enable continuous fabrication of bijel fibers.[9], [10] Characterization will be performed using confocal, optical and electron microscopy. Examples of industrial biphasic reactions e.g. hydrolysis and esterification, will be tested in homogeneous and/or heterogeneous conditions. A continuous flow reactor out of these bijels will be constructed using photolithography. The flow of fluids throughout the pore network will be realized using an electroosmotic or pressure-driven flow.

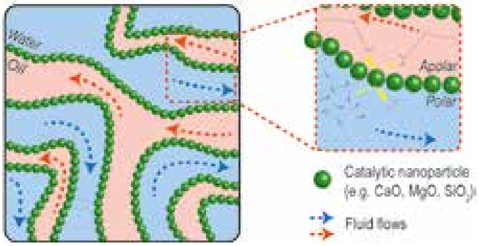

Figure 1: Schematic representation of a bicontinuous flow through a bijel network containing a catalytically active layer of NPs in an esterification of oleic acid to biodiesel. The reaction between oleic acid and (an excess of) methanol and the separation of the products methyl oleate and water occur in a single step at the liquid-liquid interface. Methyl oleate ends up in the apolar oil phase, where water and the excess of methanol remain in the polar phase. Figure and reaction inspired by ref. [4], [11].

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[9] M. F. Haase *et al.*, Chapter 6 from 'Soft Matter Series No. 10', (2020)
[10] M. F. Haase *et al.*, *Adv. Mater.* **27**, 7065–7071 (2015)
[11] S. Mohebbi *et al.*, *Fuel* **266**, 117063-1-8 (2020)

High surface area bijels for biphasic catalysis

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Bijel, Interfacial catalysis

Bicontinuous interfacially jammed emulsions (bijels) are particle stabilized bicontinuous emulsions formed by spinodal decomposition. Due to their biphasic composition and internal porosity, bijels have potential applications in catalysis [1] membrane separations [2], and energy storage. [3] Bijels are traditionally formed by phase separation of partially miscible binary liquids upon heating or cooling. [4] However, this method typically generates bijels with relatively small internal surface areas. Recently, solvent transfer induced phase separation (STrIPS) has been introduced to continuously generate bijel fibers, films and microparticles [5] (see Figure 1). STrIPS can generate bijels with much higher surface areas, potentially enhancing their performance in applications. I am investigating the formation of nanostructured STrIPS-bijels formed by the rapid stabilization of the liquid-liquid phase separation with nanoparticles.

My research analyzes the dependency of bijel formation on the ternary liquid-liquid phase equilibrium and the nanoparticle surface chemistry. To this end, I employ a combination of techniques including confocal laser scanning microscopy, scanning electron microscopy, pendant drop tensiometry, and microfluidic in-situ mechanical testing [6]. Ultimate goal of my project is to generate nanostructured bijels for applications in biphasic catalysis. The idea is to catalytically functionalize the nanoparticles within a bijel. The catalytic nanoparticles can then promote the chemical reaction of immiscible reagents within the bijel.

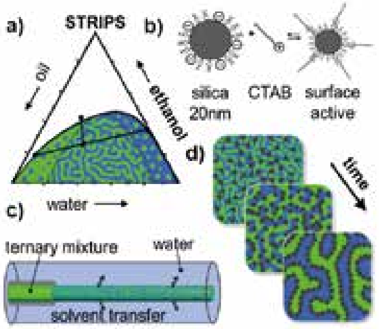

Figure 1: a) Ternary liquid-liquid phase diagram depicting regions of nucleation and spinodal decomposition. b) Surface functionalization of silica nanoparticles. c) Schematic of microfluidic bijel fiber formation. d) Schematic of interfacial jamming for bijel stabilization.

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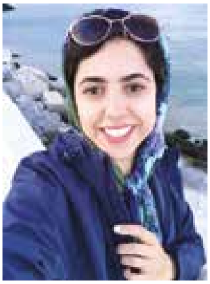
Designing iron-containing systems for food fortification



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Iron-containing pyrophosphate salts, Dissolution behavior, Food fortification

Micronutrient fortification is often carried out on food products to overcome mineral and vitamin deficiencies.[1] Among minerals, particularly iron receives significant attention since it is often deficient in the human diet.[2] However, considering the high reactivity of iron, the organoleptic properties and bioavailability of the micronutrients should be carefully balanced for successful food fortification.[3]

In this project, inspired by nature, we design mixed calcium-iron (III) pyrophosphate salts, with the general formula $Ca_{2(1-x)}Fe_{4x}(P_2O_7)_{(1+2x)}$ which are promising delivery systems for iron in food products due to their unique pH-dependent dissolution behavior. A facile and inexpensive coprecipitation method is used to synthesize calcium pyrophosphate (x=0, CaPP), iron (III) pyrophosphate (x=1.0, FePP) and four mixed salts with different x-values, which were respectively formulated as $Ca_{1.72}Fe_{0.56}(P_2O_7)_{1.28}$, $Ca_{1.70}Fe_{0.60}(P_2O_7)_{1.30}$, $Ca_{1.64}Fe_{0.72}(P_2O_7)_{1.36}$, and $Ca_{1.30}Fe_{1.40}(P_2O_7)_{1.70}$. We investigated the pH dependence of the dissolution profile of these salts in a pH range from 1-10. The results of the present study indicated that the mixed salts with Ca:Fe ratio > 1 (*i.e.*, x≤0.18) showed up to an eightfold decrease in iron solubility at food relevant pH levels (3-7) compared to FePP. Furthermore, the salts showed enhanced iron solubility, with up to a fourfold increase of soluble iron for x = 0.14 at gastric pH (1-3) compared to FePP. In conclusion, the present findings indicate that mixed Ca-FeIII pyrophosphate salts with x≤0.18 in the general formula $Ca_{2(1-x)}Fe_{4x}(P_2O_7)_{(1+2x)}$ can be potential food fortificants with reduced iron-mediated reactivity.

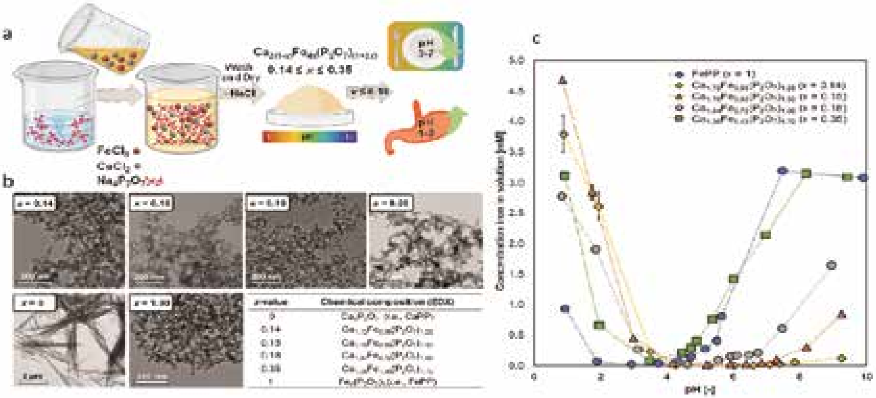

Figure 1: a) overview of synthesizing mixed calcium-iron (III) pyrophosphate salts. b) the morphology and formula of the mixed salts. c) Dissolution behavior of the mixed salts with respect to ferric pyrophosphate.

[1] J. R. Díaz *et al.*, *Eur. J. Clin. Nutr.* **57**, S70–S72 (2003)
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[3] E. J. T. McGee *et al.*, *LWT*, **89**, 756–762 (2018)

Pickering emulsion stability and rheology

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Emulsion (de-)stabilization, Optical microscopy, Rheology

Emulsions are of great importance for the oil, food and cosmetic industry. Most frequently, emulsions are stabilized with surfactants; however, such emulsions are not always stable under shear, and alternative stabilization mechanisms have therefore been intensively explored in recent years. Amongst these, particle-stabilized emulsions have attracted much attention, notably for their high stability and possible role in food applications, in the design of more environmentally friendly formulations and for the realization of high internal phase emulsions. This type of emulsion is called a Pickering emulsion [1]; particles are adsorbed at the oil/water interface with a high stabilization energy and are believed to form a continuous layer around the dispersed drops impeding coalescence and hence stabilizing the emulsion. Commonly, the stabilization is a combined effect of particle adsorption at the fluid interface and a particle network in the continuous phase; the contribution of each to the overall stability is difficult to assess. [2] We will investigate the role of particles on high internal phase emulsion stability by comparing emulsion stabilization by surfactant only, by surfactant plus particles, and finally by particles only.

The key question is how general rules can be obtained for Pickering emulsions that allow formulating stable emulsions with a desired rheology, or inversely, how flow can be used to destabilize emulsions loaded with particles.

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