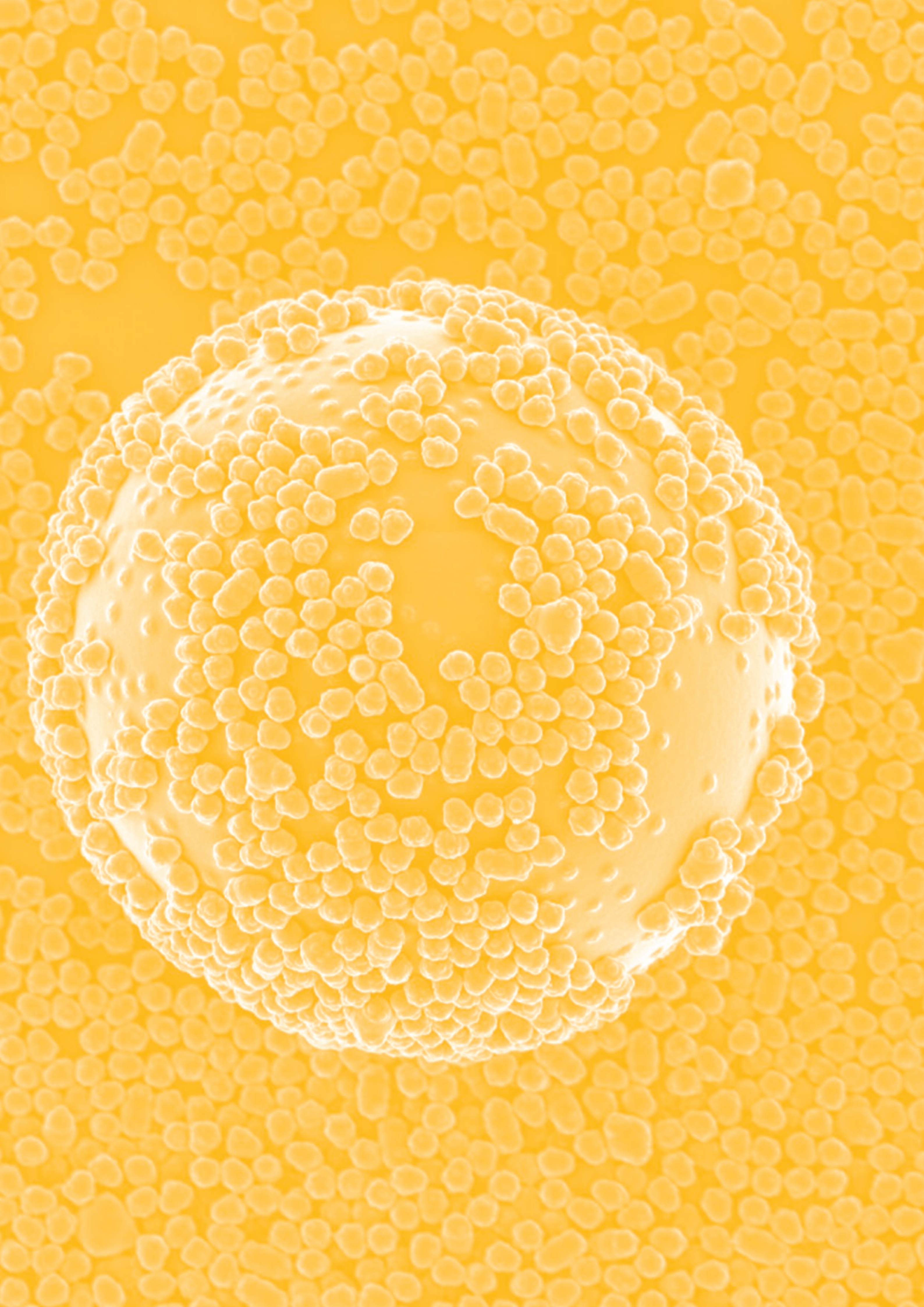
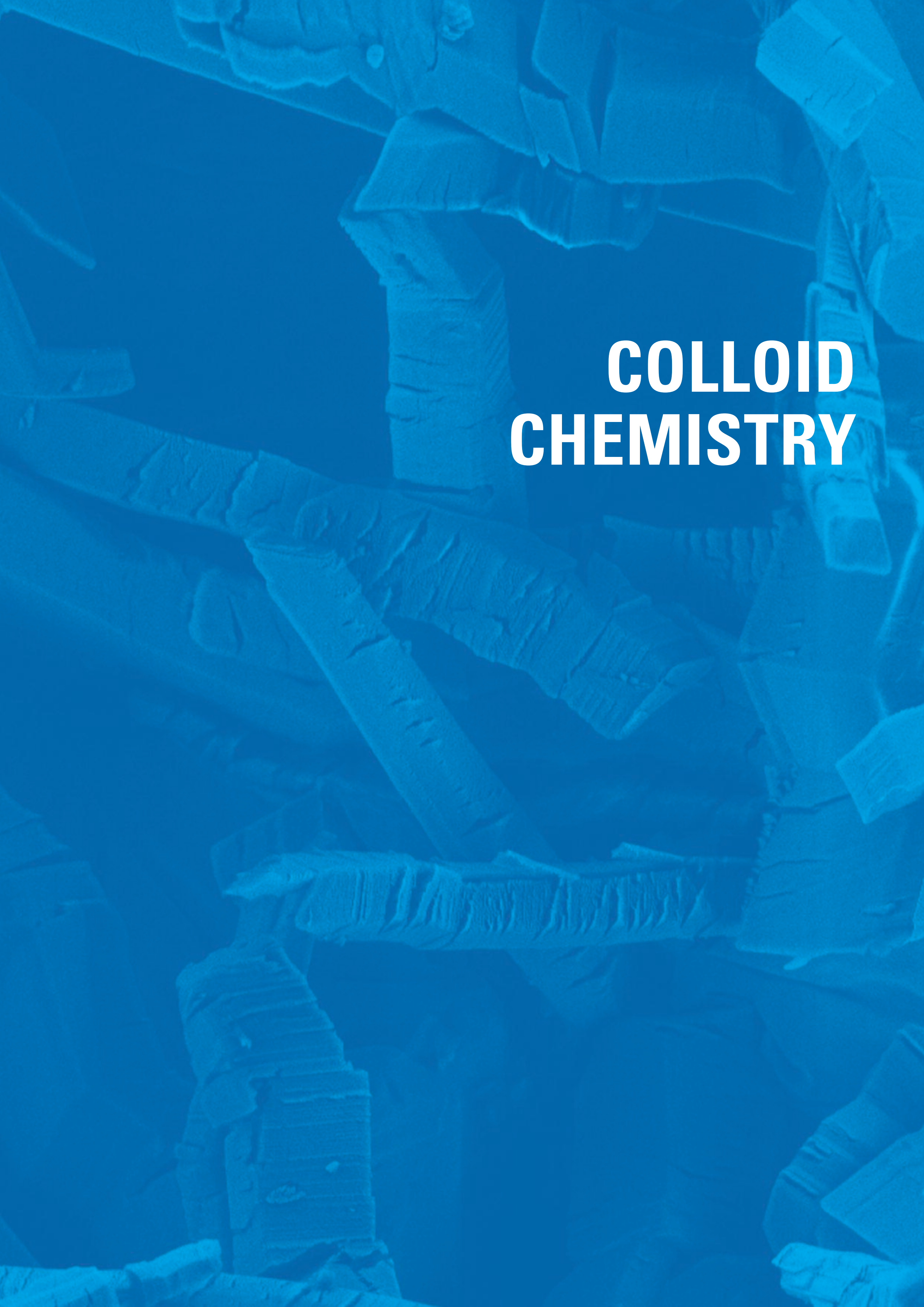




COLLOID CHEMISTRY

Research in the Department of Colloid Chemistry

Markus Antonietti 06.02.1960
1983: Diploma, Chemistry
(University of Mainz)
Thesis: Bestimmung der Diffusion von photomarkiertem Polystyrol: spezielle Systeme, chemische und physikalisch-chemische Aspekte
1985: Doctorate for natural science
(summa cum laude, University of Mainz
Thesis: Diffusion in topological constraint polymer melts with Prof. Dr. H. Sillescu
1990: Habilitation, Physical Chemistry
(University of Mainz) Thesis: Microgels – Polymers with a special architecture
02/1991: Associate Professor
(University of Mainz)
09/1991: Full Professor
(Philipps University Marburg)
Since 1993: Director
(Max Planck Institute of Colloids and Interfaces, Golm),
Full Professor (University of Potsdam)

Scientific Profile

The overall size of the Department of Colloid Chemistry has decreased due to legal changes of employment contracts to about 65 people, however still covering a broad range of research topics. The effective constituting element of the scientific activities is the "project", a structure headed by a senior scientist involving a mixture of technicians, graduate students, and post-docs (3 – 10 people). Projects are related to scientists, but usually have a temporal character of about 5 years. After this time, permanent scientists (including the director) have to redefine their profile to justify the allocation of resources. In the case of non-permanent scientists, the projects usually leave the department with the promotion of the scientist, i.e. the group leaders can continue their specific research in their new academic environment (usually as professors) without competition of the institute.

In the time of this report and following those rules, the serious changes of my department already running in the last three periods continued to take place. Dr. Menny Shalom was promoted to Associate Professor at the Ben Gurion University/Israel, and the contracts of Dr. Dariya Dontsova and Dr. Davide Esposito which were bound to ternary funding operations were running out. Dr. Tim Fellinger accepted a junior guest professorship in Gothenburg and a Professor substitution for 6 months; Dr. Jiayin Yuan went out for an Associate Professorship at Clarkson University/New York. For those, Dr. Martin Oschatz moved in with a Liebig Stipendium, Dr. Ryan Guterman and Dr. Oleksandr Savatieiev accepted the duties to continue running operations and took responsibilities of left over groups. Dr. Valerio Molinari is now in the exploration phase of a novel science experiment, the so-called "kitchen lab". I am, however, happy to have won Dr. Marc Willinger as a Senior Project Leader for the new AC-HRTEM laboratory, a 5 M operation which came into completion in 2016.

It is fair to say that a majority of the group is now still in the early phase of higher academic profiling, making the following report more concept than result oriented. This turnover of leading junior scientists is beyond typical and easy, and I would opt for some more stability after so many changes.

The following topics are currently explored within the department:

- Heterophase Polymerization (until February 2016, then retirement)
- Novel Self Assembly Polymers
- Next generation Electrochemistry materials
- Modern Techniques of Colloid Analysis
- Energy and Environmental Utilization of Carbon Nanomaterials
- Colloid Chemistry for Green Chemistry, green polymers and Biorefining, Kitchen Lab
- Artificial photosynthesis

The projects behind the headers are briefly explained below:

Heterophase Polymerization (Retirement of Klaus Tauer in February 2017)

The notation „Heterophase Polymerization" summarizes the techniques of suspension-, emulsion-, mini-, and microemulsion-polymerization as well as precipitation polymerization. Solvent is usually water. In all cases, the product is a polymer colloid or polymer nanoparticle This class of techniques, although one of the eldest in polymer science, is still most actual, as it allows the production of high polymer containing formulations in water as an environment-friendly solvent and to address nanoparticles and nanostructures on an industrial scale.

Central points of interest of the team working on heterophase polymerization are:

- Understand nucleation and particle formation for an optimal control of the particle; the experimental investigations are supplemented by theoretical and modelling descriptions *(Dr. Klaus Tauer).*
- Synthesis of complex polymer morphologies on a colloidal level (core-shell latices, hollow spheres, non-isometric particles) by a rational use of the particle interfaces and interface effects in heterophase polymerization *(Dr. Klaus Tauer).*

Novel Self Assembly Polymers

Amphiphilic polymers usually consist of components which dissolve in different media, e.g. a hydrophilic and a hydrophobic part, but this paradigm is proven to be incomplete. The newest observation in this direction is that also block copolymers without hydrophobic contrast can self-assemble to complex structures. Focal points of interest in this project group are:

- The micelle formation and lyotropic liquid crystalline phase behavior of double hydrophilic block copolymers is examined in dependence of the molecular structure, the relative amount of the different components, as well as the secondary interactions between the structure forming bio-like blocks *(Dr. Bernhard Schmidt).*
- Oligophenols are omnipresent in Nature, but less well used an examined in synthetic polymer chemistry. As polyphenols are strongly interacting with each other, with metals and with surfaces, we expect to discover "the fourth code" of polymeric secondary structure formation *(Dr. Bernhard Schmidt).* First amphiphiles with lignin fragments have been made.
- Polymer Ionic liquids represent highly polarizable surfactants which enable to solve very complicated dispersion problems, e.g. nanocarbons in water. The synthesis and self-organization of those PILs was systematically explored for the last four years *(Dr. Jiayin Yuan)*
- Polymer Ionic Liquids 2.0: Due to the promotion of Dr. Yuan, the activities are continued with *Dr. Ryan Guterman*. He is currently focusing on PILs as binders for electrodes as well as novel PIL chemistry to broaden the range of available polymer structures

Next Generation Electrochemistry Materials

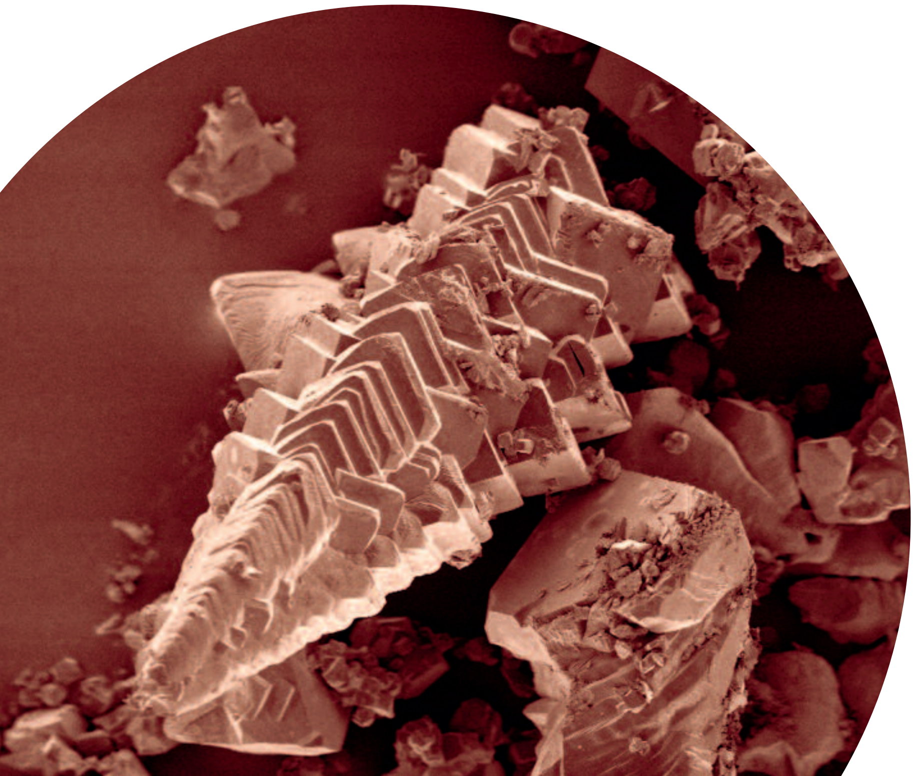
Following the project house ENERCHEM which has ran out, our department continues to take a leading role in the field of energy materials. This was also appreciated by the creation of the MaxNet, which has started in 2014 and host some of the activities described below. Hydrogen storage, better fuel cells, new energy cycles, new catalysts for more efficient processes, novel batteries, ultra-capacitors, remote energy storage, all these topics are intimately connected with the control and design of materials nanostructure. Activities based in Golm include:

- Metal free organocatalysis and photocatalysis with porous organic semiconductors: Novel synthesis schemes towards carbonnitrides *(Dr. Oleksandr Savatieiev).*
- Superhigh surface area carbons and their use for supercapacitors. Salt melt carbon synthesis and supramolecular approaches towards C_2N *(Dr. Nina Fechler)*
- New battery concepts such as the Magnesium battery rely on new solvent systems, new cathodes based on surface instead of intercalation, and of course novel solvent/ conducting salt systems. All this – with a physicochemical perspective – is handled within the new group of *Clemens Liedel*.

Modern Techniques of Colloid Analysis

All the work described above is necessarily accompanied by a considerable amount of colloid analysis which includes fully commercial techniques, but also relies on the development of new techniques or methods of preparation and data handling. The developments in this area are currently mainly focused on electron microscopy:

- Special techniques of transmission and scanning electron microscopy on soft, structured matter which are run on the base of a central service group *(Dr. Marc Willinger, Dr. Jürgen Hartmann).*
- Dynamics of growth and catalytic processes in time resolved electron microscopy *(Dr. Marc Willinger)*



Energy and Environmental Utilization of Carbon Nanomaterials

The group of *Dr. Martin Oschatz* is a rather recent addition and for the first 3 years placed by a Liebig-Fellowship. Dr. Oschatz will combine his longstanding experience on porous carbon materials from the Kaskel group with or own expertise in sustainable carbon synthesis. Projects include:

- Electrically induced gas sorption and gas separation. Similar to CDI in liquids, it is analyzed if gas adsorption can be biased by an outer potential. This should enable electroswing processes
- Superstable and non-innocent catalytic supports for electrochemistry and classical heterogeneous catalysis.

Colloid Chemistry for Green Chemistry, Green Polymers and Biorefining: Kitchen Lab

Advanced materials chemistry is still mostly based on non-sustainable resources, leading to the so-called "element crisis", e.g. the global depletion of Co, Ni, Ta, or In. Based on previous projects on hydrothermal carbonization, we carefully analyzed hydrothermal processes for the generation of value chemicals from biomass. These projects were first driven by my ERC Advanced Grant but now have reached practical matureness. This project platform includes

- Valorization of lignin via reductive hydrothermal splitting (a joint Max Planck-Fraunhofer project,
- Conversion of carbohydrates into lactic acid and other platform chemicals (Dr. Valerio Molinari, Markus Antonietti)
- Next Generation Green Polymers based on sustainable monomers *(Markus Antonietti, Dr. Bernhard Schmidt)*

These projects move the department admittedly to upstream competence, but are expected to allow a new type of organic materials chemistry by new key components.

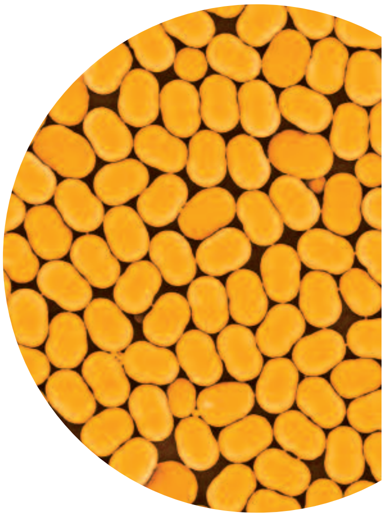
For outreach, but also for inner exploration, we just opened a so-called "Food-Lab" *(Dr. Valerio Molinari)* where typical cooking technologies are applied to the field of material synthesis. This is to be understood as the inversion of the principle of "molecular cuisine". Started as a safe place for school kids and candidates of temporal chemistry ban, it quickly turned out as a fountain of fresh processing ideas and materials. A first product is our so-called "wood remix", which is the base of a currently designed "flagship project" *(Dr. Nina Fechler).*

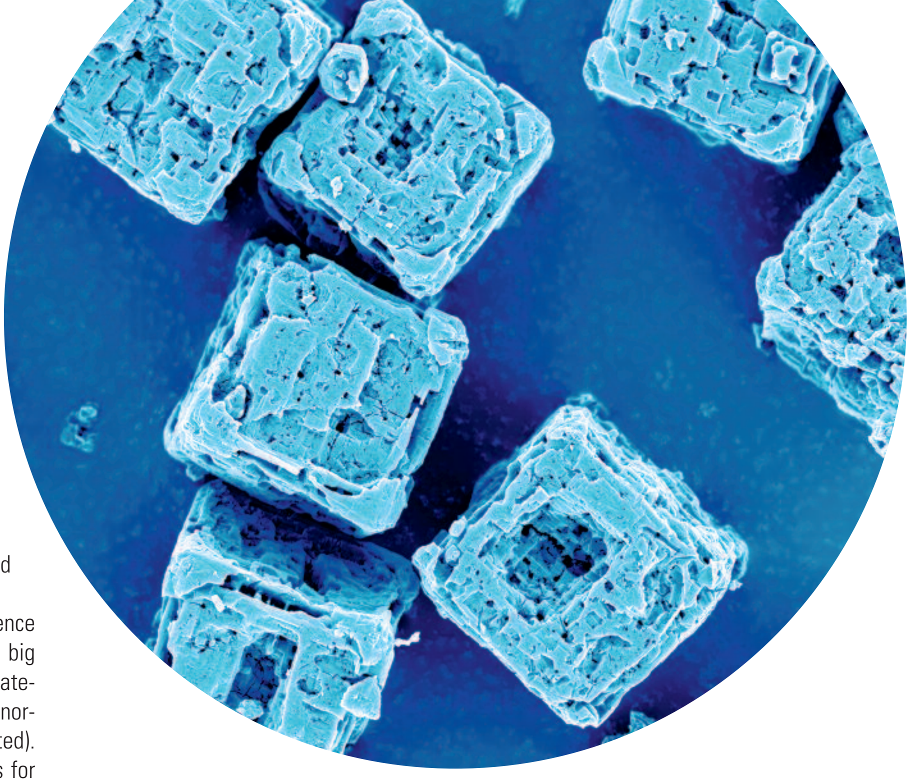
Artificial Photosynthesis

The international joint laboratory on Artificial Photosynthesis was established in July 2008 between the Max-Planck Institute of Colloids and Interfaces (Prof. Markus Antonietti) and Fuzhou University (Prof. Xianzhi Fu). The lab is now lead by Prof. Dr. Xinchen Wang, former group leader of the MPI-CI. Natural photosynthesis, the process by which green plants are converting solar energy into chemical energy, has inspired the development of artificial versions of photosynthesis, i.e. (1) the splitting of water into hydrogen and oxygen, and (2) the conversion of carbon dioxide into organics via sunlight. This was recently also successfully supported by a DFG-NSFC binational project

An important challenge in artificial photosynthesis is the development of catalysts that should be sufficiently efficient, stable, inexpensive, and capable of harvesting the abundant visible light in solar spectrum. There are many trials to establish stable systems for this purpose, mostly based on inorganic semiconductors with appropriately engineered bandgap. In our group we are investigating polymeric and organic-inorganic hybrid materials with controlled nanostructures as potential energy transducers for artificial photosynthesis for such applications as solar energy conversion, environmental purification, and organic synthesis.

- Melon, a carbon nitride polymer with graphitic structure, has turned out to be efficient for the direct splitting of water into oxygen and hydrogen. We improve the chemical structure of this polymer by copolymerization and textural control to improve light extinction and quantum efficiency of this process *(Dr. Darya Dontsova).*
- Novel nanoparticles act as cocatalysts for both water oxidation and reduction to replace the non-sustainable Pt and Ru currently used. Functional carbon nanodots and carbon hybrids seem to be unexpected promising choices *(Markus Antonietti).*
- New organic chemistry under photoredox conditions. A number of fellows are exploring the use of the as made catalysts for novel chemistry, such as photo-acetalization, Disulfide chemistry and thiamide synthesis. This is potentially to be integrated with the Seeberger department in a forthcoming joint project on the future of chemical fine synthesis.





Visions and Future Perspectives in the Director's View for the Next Years

After losing most of my more senior scientists for independent careers, I used the opportunity for a redefinition and reorientation of the department. I will have to continue the restructuration to enter a period with more coordinated research and longer term goals focused around the director and more tightly bound junior people.

Our trials to cooperate with the National Excellence Centre on Catalysis of the TU Berlin are to my opinion a big success, concerning the development of new catalytic materials and Solar Energy Usage Cascades (together with TU Inorganic Chemistry, 2 joint BMBF projects are now completed). The new projects on "Energy Materials" and "Processes for the Raw Material Change" turned out to be very timely and secured my department in the last two years a leading European role in these activities. This is also nicely reflected in many invitations for plenary and main lectures and the overall bibliometric performance. We are also seriously progressing with our activities to strengthen work projects between the departments, among them a "flow chemistry" project together with the Seeberger department, while also increased exchange on electron microscopy and mechanical testing is to be observed with the Fratzl department. Other potential projects which awaiting appropriate junior staff scientists are "carbon Q-dots" and "soil colloids".

Markus Antonietti
Director of the Department
of Colloid Chemistry

ARTIFICIAL PHOTOSYNTHESIS

Novel Approaches to Carbon Nitrides Based Photocatalysts

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1999-2006: Bachelor and Master of Chemical Technology and Engineering (with Honours) (National Technical University of Ukraine "Kyiv Polytechnic Institute", Kyiv, Ukraine)
2006-2007: Research assistant, Department of Organofluorine Compounds Chemistry (Institute of Organic Chemistry, Kyiv, Ukraine)
12/2007-2011: Doctoral Thesis: Titania based photocatalytically active layer-by-layer coatings on model surfaces and textile materials (University of Strasbourg; Institut Charles Sadron, Strasbourg, France; Clariant Produkte (Schweiz) AG, Muttenz, Switzerland)
2011: Postdoctoral Scientist (Institut Charles Sadron, Strasbourg, France)
2012: Postdoctoral Scientist Department of Colloid Chemistry (Max Planck Institute of Colloids and Interfaces)
11/2012-6/2016: Research Group Leader Department of Colloid Chemistry (Max Planck Institute of Colloids and Interfaces)

In the last years, carbon nitride polymers with a stoichiometry close to C_3N_4 attracted remarkable attention as photocatalysts for water splitting, heterogeneous catalysts for various reactions, catalyst supports, etc. Still, typical representatives possess a number of drawbacks to be improved, such as low crystallinity, high charge carrier recombination rates, low surface areas or sophisticated synthesis procedures. Instead of improving the shortcomings of the existing polymers, we rather focus on design and preparation of novel materials originally free from drawbacks, as exemplified below by poly(heptazine imides) and hybrid metal atom/carbon nitride systems.

Poly(heptazine Imides) are Newly Discovered Members of the Family of Carbon Nitride Photocatalysts

The use of *more acidic*, compared to traditional ones (e.g. melamine, urea), carbon nitride precursors in the salt melt assisted synthesis results in the formation of potassium poly(heptazine imides) (PHIK) instead of conventional LiCl-intercalated poly(triazine imides). The increased acidity of the precursor strengthens interactions between condensation intermediates and K^+ ions, improves solubility of the former, and thus changes the reaction mechanism and the structure of the final reaction products. Originally, we used substituted 1,2,4-triazoles to access these fascinating materials **[1]**. Triazole-derived PHIK products displayed high activity in the visible light driven hydrogen evolution reaction (HER); still, the crystallinity of PHIK remained moderate.

Using 3-amino-1,2,4-triazole-5-thiol as a precursor, we developed a simple *one-step* procedure to prepare carbon nitride nanocomposites containing both water reduction (exemplified by MoS_2 nanoparticles) and water oxidation (exemplified by Co_2O_3 clusters) centers **[2] (Fig. 1)**. This was achieved by the salt melt assisted condensation of 3-amino-1,2,4-triazole-5-thiol that serves as C_3N_4 polymer precursor and sulfur source, and using small amounts of $MoCl_5$ and a reactive Co_3[3,5-diamino-1,2,4-triazole]$_6$ complex for the introduction of MoS_2 NPs and cobalt species, respectively. Under optimized synthesis conditions, poly(heptazine imide) phase is fairly crystalline, while 2H-MoS_2 NPs have the beneficial geometry for hydrogen evolution with an increased number of the active edge sites. The use of the *reactive* Co precursor results in homogeneous incorporation of Co_2O_3 clusters in the composite thus creating the active sites for oxygen evolution.

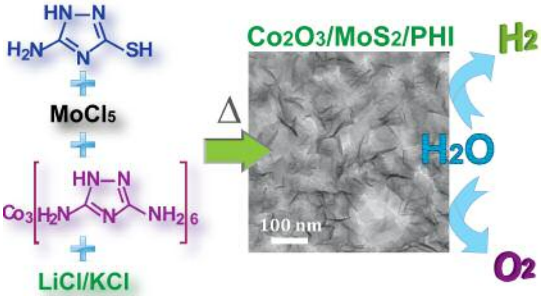

Fig. 1: Schematic of preparation and application of poly(heptazine imide) based composites in water splitting upon visible light irradiation.

More recently, we found that using the *more acidic* compared to 1,2,4-triazoles, amino-tetrazole as a precursor enables preparation of highly crystalline PHIK, in which the crystallinity extends over hundreds of nanometers enabling efficient electron/hole transport **[3]**. The crystal structure of products can be tuned by simple variation of the preparation conditions, leading to the alteration of their electronic properties (conduction and valence band positions). The poly(heptazine imide) works as a 'sponge' for K^+ ions enabling higher or lower ion intercalation. The conducted ^{13}C and ^{15}N SS-NMR and HR-TEM studies provided new insights into the PHIK structure depicted in **Fig. 2a** thus extending previous knowledge about this intriguing newly discovered class of materials.

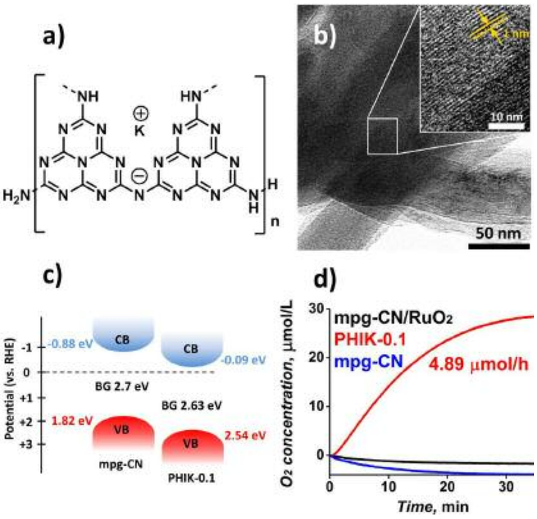

Fig. 2: Chemical structure of potassium poly(heptazine imide) (a); TEM image of a sample tetrazole-derived product (b); schematic illustration of the electronic band structures of conventional mesoporous graphitic carbon nitride (mpg-CN) and PHIK (c); visible light driven oxygen evolution by PHIK and reference materials (d).

The improvement of the structural order in PHIK resulted in much higher compared to known carbon nitrides, VB potentials in solids, 2.5 eV vs. 1.8 eV **(Fig. 2c)**. Thus, in addition to high activities in HER, tetrazole-derived PHIK are shown to photocatalytically liberate oxygen from water with high efficiency, without any metal co-catalysts **(Fig. 2d)**.

The aberration corrected high resolution electron microscopy studies of tetrazole-derived PHIK revealed that the nanostructure of the materials is represented by *columns* of heptazine units stacked on top of each other (stacking distance is ~0.3 nm) and *channels* occupied by potassium ions. The channels are located ~1 nm apart from each other **(Fig. 3a)**. The potassium ions in the channels can be easily exchanged by protons, or by a variety of alkali (Li, Na, Cs), earth alkali (Mg, Ca) and transition (Ni, Co, Ag, Zn) metal cations, keeping the stacked aromatic structure essentially intact, as illustrated in **Fig. 3b**. Such behavior is a typical feature of organic zeolites. The ion exchange causes alterations in the conductivity and electronic properties of the materials leading to increase or decrease of their photocatalytic performance, as it was exemplified by photocatalytic water reduction **[4]**.

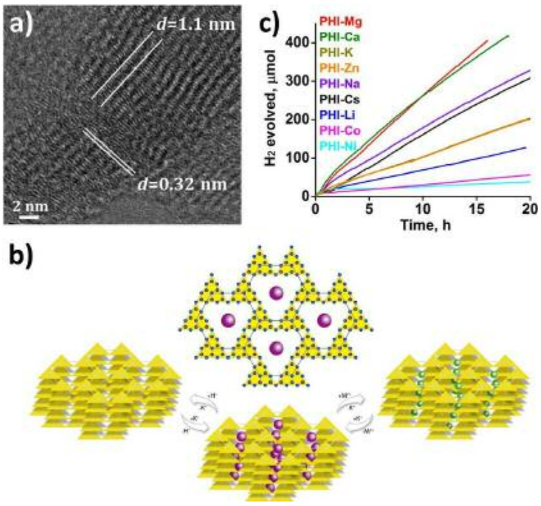

Fig. 3: HR-TEM image of tetrazole-derived potassium poly(heptazine imide) (a); idealized poly(heptazine imide) network structure illustrating proton–ion and ion–ion exchange (b); time dependent hydrogen evolution over poly(heptazine imide) salts upon irradiation with visible light (c).

The earth-alkali metal containing poly(heptazine imides) show a significantly improved activity and a more than twice higher hydrogen evolution rates compared to the pristine potassium salt **(Fig. 3c)**. The highest activity of 25.1 µmol H_2/hour is measured for *magnesium* salt that can be attributed to its high structural order and effective charge separation. The last example reveals the similarity of poly(heptazine imides) with chlorophylls where nature also uses magnesium ions to achieve the most efficient light harvesting. The ability of ion exchange positions poly(heptazine imide) as a solid state ion conductor further strengthening its application potential.

Single Metal Atoms/Graphitic Carbon Nitride Catalytic Hybrid Systems

In order to obtain functional carbon nitride-based composites for various catalytic applications, not limited to photocatalytic ones, we elaborated a general strategy to obtain a *joint electronic system with a shared electron orbital structure* consisting of atomically dispersed metal, here exemplified by silver, and carbon nitride polymer, by co-polymerization of the reactive silver tricyanomethanide with the carbon nitride precursor, cyanamide. This method avoids the drawbacks of the previously reported approaches of metal doping, but offers the advantage of extra-electron density present at carbon and nitrogen atoms resulting in the alteration of the semiconductor properties and the increase of the negative surface charge. The benefits of the developed doping method are illustrated in two applications: the photo-assisted water reduction (after further Pt NPs deposition) and the selective hydrogenation of 1-hexyne, where atomically dispersed Ag-doped carbon nitrides show an enhanced performance in comparison with other conventional Ag-based materials **(Fig. 4) [5]**. By optimizing synthesis conditions, Pd **[6]**, Ir, Pt and Au **[7]** were atomically doped into carbon nitrides, and the catalytic properties or the resulting materials were evaluated.

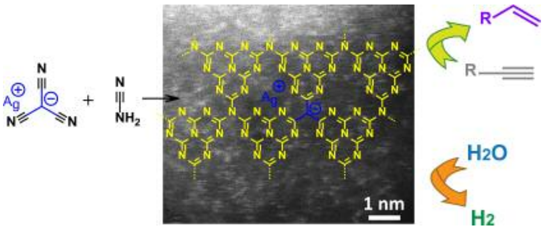

Fig. 4: Schematic of synthesis, structure and applications of a hybrid Ag@mpg-CN catalytic nanocomposite.

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BIOMASS CONVERSION INTO BUILDING BLOCKS FOR COLLOIDS

Biorefinery and Sustainable Chemistry

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2004: Visiting researcher at University of Leiden, Netherland (Erasmus Project)
2006-2011: PhD Studies: Department of Chemistry, ETH Zürich, Switzerland with a research stay at the MPI for Colloids and Interfaces, Potsdam, Germany
2011-2012: Postdoctoral Research: MPI for Colloids and Interfaces, Potsdam, Germany
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Modern society is still heavily dependent on fossil resources for the generation of fuels, chemicals and pharmaceuticals. Unfortunately, the last decades have witnessed a constant depletion of traditional fossil feedstock. In addition, the global use of non-renewable resources has been responsible for a constant increase in environmental pollution. In this scenario, modern society is facing the challenge to provide solutions for a sustainable and environmental friendly development. In the last decades, the scientific community has identified biomass and food waste as promising feedstocks for the generation of fuels and commodity chemicals. The valorisation of renewable feedstocks in a biorefinery is analogous to that of classical refineries, which convert fossil resources (oil) into higher value products (fuels and chemicals). To date, examples of biorefineries for the production of energy (by thermal methods), or fuels (by biotechnological approaches) have appeared. Nevertheless, the *selective generation of bio-based fine chemicals and building blocks from biomass* using chemical strategies is still in its infancy, and its success will strongly depend on the development of efficient catalytic methodologies. *The main objective of our group is the development of successful strategies for synthesis of bio-active compounds and monomers using biorefinery-derived synthons as the starting materials.* We are currently articulating our research around three major thematic areas:

1. the development of solvo(hydro)thermal methods for biomass deconstruction, which enable the conversion of polysaccharides and lignin into an array of useful primary building blocks and platform chemicals;
2. the development of novel sustainable catalytic methods for the upgrade and functionalization in microfluidic reactors of primary biomass derived substrates;
3. the synthesis of value-added products on the basis of sustainable building blocks obtained through biorefinery conversion schemes.

1. Solvo(Hydro)thermal Deconstruction of Biomass

Lignocellulosic materials are rather heterogeneous in nature and are mostly composed of polysaccharides, usually accounting for 60-80% of the weight, and lignin (15-30%). The entry step in a biomass conversion scheme should enable the separation of the carbohydrate portion of the biomass from the lignin one. In this regard, organosolv methods, which consist in the treatment of biomass with organic solvents at elevated temperatures, have found broad application. Nevertheless, this approach has been aimed at the sole isolation of the lignin fraction. In order to improve the efficiency of these kinds of treatments, we design new methodologies that allow for the simultaneous isolation of an upgraded polysaccharide fraction. For example, we identified conditions for the alkaline hydrothermal treatment of sugars and biomass which are highly selective for the formation of lactic acid, a very important platform chemical for the preparation of biodegradable plastics **[1]**. This strategy has proven successful when applied to the conversion of raw biomass on a 40 grams scale. During the treatment of raw biomass, in addition to lactic acid, lignin can also be isolated, suggesting the possible use of this convenient method as entry point for new biorefinery schemes.

Besides alkaline treatments, complementary acidic hydrothermal methods, which usually results in the formation of C5 scaffolds, are also being explored. For instance, we optimized a method for the conversion of cellulose into levulinic acid, a very versatile platform chemical, which was subsequently hydrogenated with Raney-Nickel to afford γ-valerolactone **(Fig. 1) [2]**. The successive functionalization of γ-valerolactone via α-methylenation was also accomplished, in order to obtain a monomer suitable for radical polymerization. **[3]**

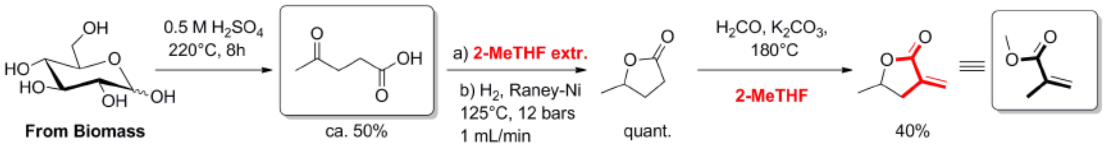

Fig. 1: Example of the synthesis of monomers from sugar via hydrothermal deconstruction and upgrade of primary building blocks.

Finally, the preparation of latex particles on the basis of such monomer was investigated as a proof of principle. The whole synthetic route showcases an example of integrated refinery scheme capable of converting lignocellulosic feedstock into value-added materials, as already shown schematically in **Figure 1**.

One of our future objectives in this area will be the screening of different solvothermal conditions in order to widen the spectrum of possible platform chemicals targets.

2. New Catalytic Continuous Flow Methodologies for the Upgrade of Bio-derived Molecules

Many of the primary products of the hydrothermal treatments of biomass can be conveniently upgraded into different platform chemicals by straightforward catalytic transformations. To reach this goal, we focus on the development of new continuous flow methodologies using supported catalysts. Traditionally, expensive and rare elements belonging to the platinum-group metals have been proposed as catalysts for such transformations. However, the use of inexpensive and abundant elements, for example iron and nickel, appears a good option to achieve the production of bio-derived chemicals in a more sustainable fashion. Carbon supported metals have been successfully applied as catalysts in the field of hydrogenolysis and hydrogenation. With this in mind, we prepared carbon supported Ni-Fe alloys by simple impregnation of cellulose from biomass followed by carbothermal reduc-

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tion **[4]**. This form of reductive treatment has proven ideal to generate carbon encapsulated nanoparticles characterized by high activity and stability. In particular, this material served as an optimal catalyst for the continuous flow reduction of a variety of biomass-derived compounds. More recently, we extended this approach to achieve the reductive amination of biomass molecules, as a general step for the preparation of intermediates in the synthesis of bioactive *N*-heterocyclic compounds **(Figure 2)**. **[5]**

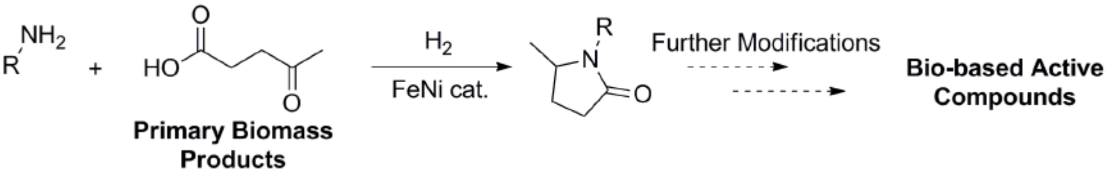

Fig. 2: Example of reductive amination as a key step for the preparation of bio-based active compounds.

In a complementary project we are pursuing the development of methodologies for the hydrogenolysis of aryl ethers, the most abundant type of linkages in lignin. We have recently showed how titanium nitride obtained as colloidal dispersion on amorphous carbon can be efficiently used as support for nickel nanoparticles,**[6]** leading to the preparation of a new composite with a high reactivity for the continuous flow hydrogenolysis of different aryl ethers and model lignin fragments. Currently, we are investigating in detail the hydrogenolytic depolymerization of lignin, which can afford a library of highly valuable aromatics scaffolds.**[7]** Lignin derived aromatics offer a unique set of functionalities (mostly polyphenols with a common phenyl propane backbone) that can give access to a well distinct chemical space upon functionalization, characterized by specific bio-activity (e.g. antioxidant activity).

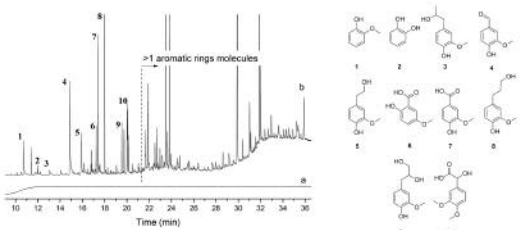

Fig. 3: Representative chromatogram of lignin hydrogenolysis over TiN-Ni for the preparation of bio-based aromatic compounds

In a series of different projects, we also exploited lignin fragments and oligomers for the preparation of porous carbons as support for heterogeneous catalysts **[8]** or nitrogen doped carbons as efficient electro-catalysts. **[9]**

3. New Value-Added Sustainable Chemicals

On the basis of the pool of molecules which can be obtained via biomass deconstruction, we design green strategies for the synthesis of sustainable building blocks and platform chemicals that can find application in polymer science and chemical biology. One of our areas of interest is the production of sustainable *N*-heterocyclic compounds. However, the synthesis of nitrogen-containing heterocycles from lignocellulosic sources remains elusive due to the lack of nitrogen in this row material. Complementing lignocellulose-derived molecules with other renewable *N*-containing precursors can sensibly increase the chemical space accessible in a sustainable manner. In this regard, amino acids have been evoked as interesting candidates. One of our first goals in this direction was the development of green synthetic methods to access sustainable imidazolium ions, which could be further transformed into ionic liquids. During the synthesis of lactic acid, pyruvaldehyde was identified as a valuable sustainable synthon **[1]**. This and other renewable dicarbonyl compounds were exploited to synthesize a library of disubstituted imidazolium ions in combination with natural amino acids by using a green modification of the Debus-Radziszewski synthesis **(Fig. 4) [10]**. The obtained compounds have proven as versatile building blocks for the preparations of ionic liquids by means of a new continuous hydrothermal decarboxylation method developed in our laboratory. This new method showed a great potential for the generation of a new family of ionic liquids that are derived exclusively from renewable precursors.

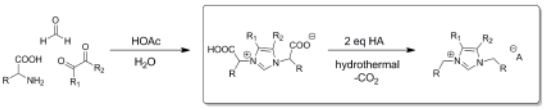

Fig. 4: Synthesis of imidazolium compounds from renewable starting materials.

Some of the so-prepared ionic liquids are under investigation as reaction media for cross coupling reactions as well as cellulose and biomass dissolution **[11]**. Recently, we employed a similar strategy also for the preparation of bio-based pyridinium zwitterions and ionic liquids using furfural (derived from sugars) and amino acids as the starting materials **(Fig. 5).[12]**

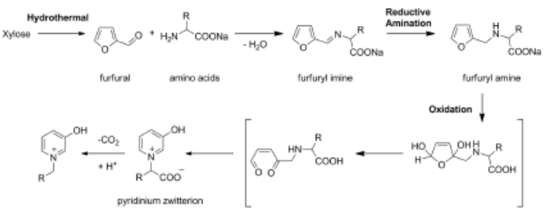

Fig. 5: Synthetic strategy for the preparation of pyridinium compounds from renewable starting materials.

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RESEARCH COORDINATOR

Supramolecular Porous Materials

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Scientific questions have become very complex and require close co-working of disciplines, research institutions and industry. However, such structures demand for careful communication and organization. Here, we believe that affiliation to both science and communications infrastructure is helpful to catalyse projects. Therefore, I decided to take the venture on this still emergent career path and operate as Research Coordinator employed by the MAXNET Energy.

Duties include the coordination of (internal) projects with the other partners of MAXNET Energy. Furthermore, in order to understand the needs and to stay active in the communication stream, I also work on my own research topics together with my small group, often in close collaboration with partner institutions. This allows me to further develop my scientific profile which is also a prerequisite for an effective coordination of research.

In this context, I complete my Master degree in Science Marketing at the TU Berlin.

A) Research Coordination

The MAXNET Energy pools knowledge and activities of eight different MPIs and tries to establish accelerated progress in the field of sustainable materials for energy conversion. Here, materials, measurement setups and theory for water splitting are the main focus.**[1]** Within these activities I'm responsible for the communication and matching of projects between the MAXNET Energy consortium and activities of our department.

B) Research Topics

In my group we aim to make use of rational and facile synthesis schemes towards functional porous carbon materials. **[2]**

On the one hand, salts turned out to be highly versatile alternatives for the generation of nanoporous structures. In this regard, we also develop methods to make the carbons more processable.

On the other hand, we follow the supramolecular approach where we currently make use of preorganization schemes mediated through strong but non-covalent and thus reversible interactions. Recent activities include:

- use of precursors with the ability to form hydrogen-bond structures resulting in eutectic mixtures or crystals. These intermediates can then form pre-defined, more ordered nanostructured carbons with unusual elemental composition and properties
- application of natural (poly)phenols in combination with soft-templating agents to form functional porous carbon monoliths and films
- coordination of phenols with a specific structure and metal ions to form crystalline oxocarbon metal complexes. These crystals can be further converted into porous carbons or metal-carbon composites with high degree of chemical surface functionality and preservation of the original crystal morphology such as micro cubes or small plates.

Nanoporous Carbons

Functional carbons and composites entered everyday life as they possess a variety of important properties while costs are rather low.

The final materials properties such as chemical and thermal stability, surface functionality or morphology are governed, besides others, on the molecular as well as mesoscopic level. The incorporation of heteroatoms such as nitrogen into the carbon lattice, metals or porosity turned out to be highly powerful.

However, opposed to inorganic systems the rational synthesis of functional carbons is still complicated. This is mainly related to the common necessity of high temperature treatments which essentially hinder external control during main phases of the synthesis. Therefore, approaches to circumvent this limitation are needed.

Here, we see one possibility in the "encoding of functionality" in the precursors, i.e. as much information as possible is already inherently present in the starting material. More specifically, the pre-setting/introduction of periodic binding motifs in the binding pool of carbon will lead to mosaic-like functional patterns. In this regard, dynamic processes such as (natural) assembly and bonding schemes offer internal control where especially hydrogen-bonds are convenient as they are strong but reversible at the same time.

Salts

In order allow reversibility also at higher synthesis temperatures, we invented a new tool called „salt templating".**[3]** The general concept is based on crosslinking of a precursor in the presence of a molten salt phase which simultaneously acts as solvent and template. Contrary to current methods, it is possible to proceed in a single-step synthesis, while the porogen can easily be removed by washing with water and in principal be recovered afterwards for further use.

Carbons from Eutectic Mixtures and Crystals

We found that complexation of quinones and phenols with urea leads to liquid monomer mixtures upon gentle heating with deep eutectic behaviour **(Fig. 1a)**. **[4]** These liquids can then be converted to carbonaceous nano architectures with well-defined nitrogen heteroatoms via condensation rather than pyrolysis, i.e. the formation of pyrazinic nitrogen sites in unusually high occurrence **(Fig. 1b)**. Due to the good processability and wettability of these liquid mixtures, this approach can furthermore be combined with various structuring methods such as templating, spin-coating and monolith formation **(Fig 1c)**.**[5]**

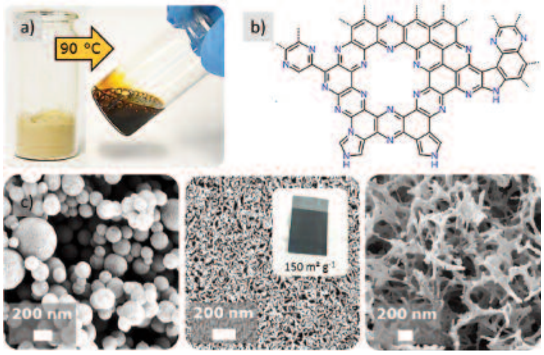

Fig. 1: a) Liquid eutectic carbon precursor mixture from heated phenol-urea powders, b) structure of the final carbon C_2N and c) Scanning Electron Microscopy images of differently processed carbons.

Additionally, depending on the quinone/phenol used we observe an ordering of the eutectic mixtures, i.e. liquid crystalline-like phases are generated which eventually contribute to the preservation of order and patterns in the final carbons. This can be pushed to the formation of actual solid crystals which then guide the final material morphology e.g. to sheets or hollow tubes **(Fig. 2)**.**[6]**

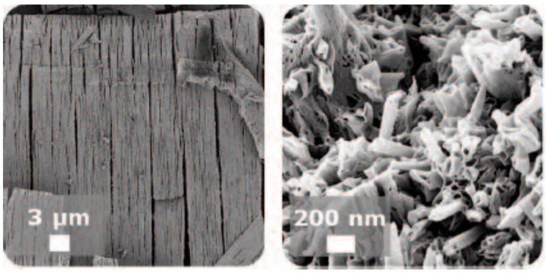

Fig. 2: Scanning Electron Microscopy images of C_2N carbons made from crystalline phenol-urea precursors.

When choosing educts without C-H bonds, the products can be generally described as a disordered version of “C_2N”. It can be expected that the resulting family of N-modified carbons will effectively complement N-doped carbons and carbon nitrides in their electronic, (electro)catalytic, and sorption applications.**[7]**

Design of Oxocarbon Metal Complexes

In the case of metal coordination with ketones and organic acids, it is possible to first form macroscopic crystalline materials which can then be further converted to the respective carbon **(Fig. 3a)**.**[8]** Depending on the nature of the precursor, metal and reaction conditions, the morphology as well as porosity of the final material can be tuned. It is to be noted that the initial macroscopic structure of the crystal is retained in the final carbon which allows for convenient shaping and setting of materials properties, in spite of the applied high temperature process. It can be envisioned that structures like cubes can further orientate based on their shape to constitute network structures with hierarchical pores **(Fig. 3b)**.**[9]** This makes such materials attractive for applications where high surface areas and mass-transport in powders are important.

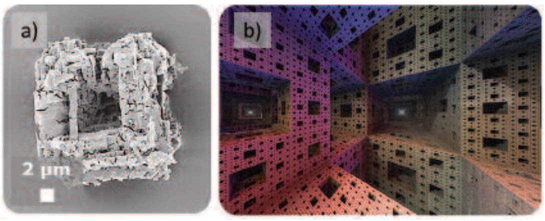

Fig. 3: a) Porous carbon cube made from an oxocarbon metal complex, b) sketch of potential 3D architectures built from porous cubes.

All these processes can be also extended to natural phenols and ketones broadening available structures while staying sustainable. With such methods in hand, it is our intention to establish a platform of facile, scalable and processable tools for the rational design of carbon nanostructures and composites.

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CARBON MATERIALS AND ELECTROCHEMICAL ENERGY APPLICATIONS

Novel Nanochemistry towards Improved Electrodes

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Introduction

The versatility of carbon materials in their physical and chemical properties together with the possibility to form and shape the morphology of carbon materials into 1D, 2D and 3D as well as micro-, meso- and macroporous structures make them indispensable for crucial technology related to new and sustainable energy schemes. Here the differentiation of physical effects (*e.g.* due to specific electronic properties) and chemical effects (due to specific surface compositions) is a difficult task. In electrochemical energy applications, where performances are often defined by accumulation or conversion of electroactive species, the influence of the morphology dictating the mass-transport properties additionally overlays such effects. The identification of the origin of performance variations is therefore even more difficult. In the "Carbon and Energy" group we are aiming to develop preparative methods to generate pores (porogenesis) and modify the porosity in carbon materials without affecting the surface chemistry and *vice versa* to elucidate structure-performance relationships in topical energy application such as fuel cells, lithium-sulfur (Li-S) batteries and lithium-oxygen (Li-O_2) batteries.

1) Salt-Templating to Ionothermal Carbonization: Carbons with Taylor-made Porosity

Recently the use of inorganic salt melts for the preparation of porous carbons has gained a lot of attention in the scientific community.**[1-4]** We previously reported on a novel one-step salt templating carbonization route using inorganic salt melts to prepare highly nanoporous nitrogen doped carbons (NDCs) from thermolysis of carbonizable ionic liquids.**[5]** The ionic liquids were used as precursors as they form homogeneous mixtures with the inorganic salt melts until the carbonization of the organic phase initiates nanoscopic phase separation (**Fig. 1a**). Aqueous removal of the inorganic salt phase after the carbonization creates nanoporosity. The actual size of the pores increased the lower the melting point of the used inorganic salts was. This trend was rationalized by separation kinetics *via* longer demixing times or lower viscosity, respectively. In a recent work we investigated the relation of the inorganic salt composition on the porogenesis in more detail for a biomass-derived nitrogen-rich carbon precursor adenine.**[6]** Stepwise increase of the NaCl fraction in NaCl-$ZnCl_2$ mixtures revealed a couple of interesting facts. 1) Very fine tuning of the pore size distribution could be realized by incremental changes in the NaCl fraction **(Fig. 1b)**. 2) The average pore size increases with increasing melting points of the inorganic salt mixture, and 3) for lower NaCl fractions a sudden loss of porosity is observed. The fine tuning of the porosity of carbon materials by simple means, like the precursor salt ratio, allows for simple access to taylor-made carbons, adapted precisely for the application addressed

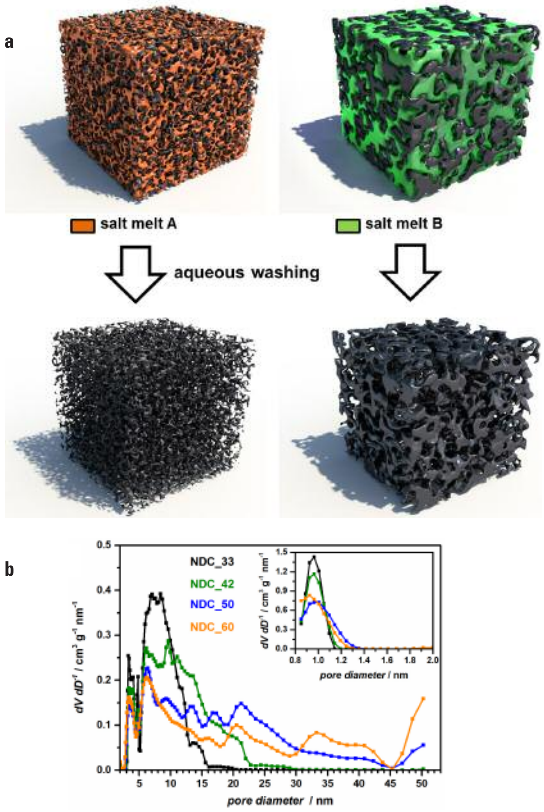


Fig. 1: a) Scheme of the pore synthesis of carbon materials by carbonization of organic matter in presence different inorganic salt melt A and B (ionothermal carbonization). b) pore size distributions for adenine-derived carbon in NaCl-$ZnCl_2$ mixtures (in NDC-XX, XX stands for {mol%NaCl} (Fig. adapted from ref ***[5]****).*

We extended the initial concept of ref.5 to glucose-derived carbon, where we obtained a linear relationship between specific surface area and fraction of KCl in KCl-$ZnCl_2$ mixtures.**[7]** In case of the adenine-derived carbons we discovered a strong pore size effect in the electrocatalytic activity of the obtained carbons **(see section 2)**. The other observations clearly point to an interplay of the inorganic salt with the organic precursor, which was previously "masked" by the very similar properties of the different ionic liquids. In fact the inorganic salt melt can be – in agreement with the original work, regarded as a high temperature solvent in the process. In this light pore generation can generally occur by means of dissolution/dispersion of the organic phase inside the salt melt or dispersion of the salt melt inside the organic matter. This insight improves the understanding of the sometimes more and sometimes less successful formation of biomass-derived activated carbons using $ZnCl_2$, that is a dispersion of nanoscopic $ZnCl_2$ droplets inside the carbonized biomass precursor. **[8]**.

Improvement of current "activation" protocols can therefore be expected from adaption of the salt composition to the biomass properties and *vice versa*. Together with the "Biorefinery and Sustainable Chemistry" group we optimized the introduction of porosity and surface area throughout carbonization of the highly abundant natural biopolymer lignin.**[9]** The carbonization of nitrated lignin (NL) in a 1:5 weight mixture with eutectic KCl-$ZnCl_2$ at 850 °C under inert gas flow lead to a nitrogen doped micro and mesoporous carbon (NL-C) with 4.8 %N and 1600 m^2 g^{-1} specific surface area. The cheap, biomass-derived material performed comparable to state-of-the-art metal-free (NDCs) and iron-containing carbon (FeNDCs) electrocatalysts in the important oxygen reduction reaction (ORR), which for instance restricts today's fuel cell performances **(Fig. 2)**.

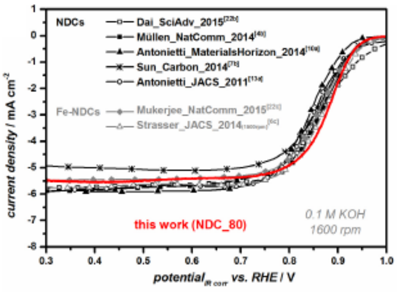
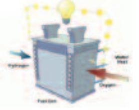


Fig. 2: Comparison of the rotating disk polarization curve (ORR in O_2 saturated 0.1M KOH) of NL-C with different literature benchmarks for non-noble metal catalysts (Fig. adapted from ref. ***[9]****).*

2) Mass-Transport Conditions are Crucial in Many Energy Applications

In electrochemical energy applications very challenging morphological electrode conditions are faced. In context of fuel cell electrodes this is typically named as three-phase boundary problem, due to the necessary spacial coincidence of the solid electrode/catalyst, the gaseous reactants and the solid electrolyte. The mechanistically related next generation battery concepts of Li-S batteries and Li-O_2 batteries even show additional deposition of the solid products on top of the electrode/catalyst (Li_2S or Li_2O_2), *i.e.* a four-phase boundary. The deposition of discharge products is herein blocking the active site and limits performances. Moreover the reaction kinetics are strongly affected by the mass transport properties of the electrode, e.g. the delivery of reactants. In our research in 2016 we came up with a few concepts on how to improve the device performances with morphologies for improved mass-transport characteristics, shown in examples for 1) fuel cells, 2) Li-S batteries and 3) Li-O_2 batteries.



The previously mentioned fine tuning of pores of ionothermal NDCs (see section 1) revealed a strong limitation of ORR performances due to the presence small bottle-neck pores. Chemically identical carbon materials showed clearly improved performance *via* opening of nanoscopic bottle-neck pores despite a clear reduction of active surface area **(Fig 3.)**. These results motivate the revisiting of the pore systems of the currently best electrocatalysts with a potentially large space for improvement of ~100 mV (*i.e.* ~8 %).**[6]**

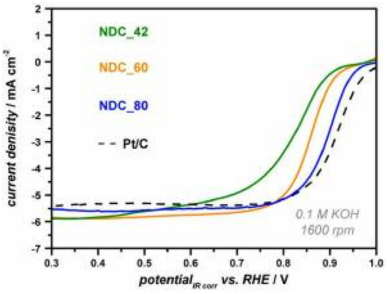


Fig. 3: Comparison of the polarization curves (ORR in O_2 saturated 0.1M KOH) of adenine-derived NDCs with different pore size distributions ***(see partly in Fig. 1)*** *and with the platinum on carbon benchmark catalyst. The respective active surface areas in m^2 g^{-1} are ~2800 (NDC_42), 2550 (NDC_60) and ~1750 (NDC_80). (Fig. adapted from ref.* ***[6]****.)*

Limited ion wiring due to reduced electrolyte wetting in Li-S batteries was shown to allow for the direct conversion of Li_2S to S_8, bypassing the formation of parasitic polysulfides that cause the most severe downside of this technology – the strong capacity fading. The supply of ions was limited by a nitrogen doped carbon layer surrounding the Li_2S particles. A peculiarity here is that the carbon layer was also used as a high temperature reducing agent of lithium sulfate nanoparticles in the synthesis to obtain the desired Li_2S nanoparticles **[10].**

Vertically aligned carbon nanosheets (CNS) display advantageous mass-transport properties due to their open card-house structure.**[11]** The material can act as an efficient ORR catalyst *e.g.* in Li-O_2 batteries. Electrodeposition of transition metal hydroxide ($M(OH)_x$) nanoparticles creates a nanocomposite with bifunctional catalytic properties, because the $M(OH)_x$ act as catalyst for the reverse reaction (oxygen evolution) that is crucial for the recharging of the battery (Fig. 4). A very interesting effect herein is that the polar discharge product (Li_2O_2) is deposited directly on the hydroxide particles, *i.e.* the catalyst for the recharging, instead of blocking the active discharge sites.

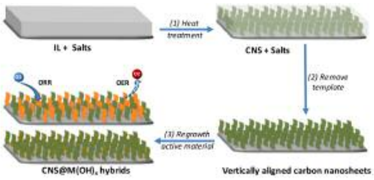


Fig. 4: Scheme of the bifunctional nanocomposits of vertically aligned CNS with $M(OH)_x$ with enhanced mass-transport properties and selective deposition of the discharge product (Li_2O_2) on the $M(OH)_x$ catalyst for the recharging.

The possibility for the discharge product to form hydrogen bonds with the transition metal hydroxides mediates nucleation directly on the recharge catalysts leading to very high capacities because of the "clean" catalyst surface.**[12]**

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MODERN TECHNIQUES OF COLLOID ANALYSIS

Electron Microscopic Studies of Colloidal Systems and Interfaces

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The study and the understanding of structure/property, structure/function and chemical synthesis/structure relations of both synthetic and biological colloidal materials are important for the development of new technologies and materials.

Synthesis of bio-inspired particles, inorganic nanoparticles and organic-inorganic hybrid materials, nano-porous carbon, functional carbonaceous materials, the preparation of polymer particles, biomimetic materials and hybrid materials, membranes, emulsions, active coatings and interfaces and functional supramolecular organizates are in focus on the interdisciplinary research in the institute.

Transmission electron microscopy, high-resolution scanning electron microscopy and environmental electron microscopy are suitable techniques to determine the characteristic structural parameters such as the shape, size and size distribution of colloidal particles and the pore size of mesostructured networks, the diameter of nanofibrills, the spatial arrangement of nanoparticles with a high electron optical resolution.

Using cryo-scanning electron microscopy the internal morphological structures of aqueous systems like concentrated oil/water emulsions can be characterized. The combination of energy-dispersive X-ray spectroscopy and high-resolution scanning electron microscopy is a powerful analytical tool to determine the local chemical composition and the spatial elemental distribution on surfaces and interface structures of solid materials.

As a central service lab the electron microscopy group performs scientific routine measurements for the whole institute, which are demonstrated in different reports of this issue. Because of the organization of the institute, there is a close collaboration with other departments of our institute, but also with the Max Planck Institute of Molecular Plant Physiology and the University of Potsdam.

Some of the interesting results of electron microscopic investigations are presented here.

In general the aqueous hetero-phase polymerization is used to form stabile solid colloidal polymer particles as single spheres. The free radical polymerization variant allows the synthesis of block copolymers. Thus, both hydrophilic N-isopropylacrylamide (NIPAM) and hydrophobic monomers styrene can be added in subsequent polymerization steps offering a wide variety of possible block copolymer structures and particle morphologies **[1]**. A peculiar particle morphology was obtained if instead of a hydrophilic polymer, hydrophilic molecules such as β-cyclodextrin (β-CD), sucrose, glycerol, and other low molecular weight alcohols (ethanol and 1-pentanol) are used as reductant. Electron microscopic investigations revealed the fine grained morphology of stable colloidal clusters (multiple suspension particle (MSP) morphology) with subtle differences depending on the particular molecular structure of the reductant **(Fig.1. a,b)**.

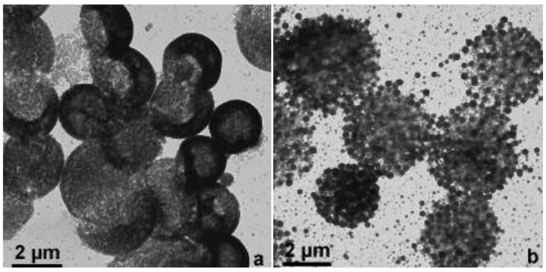

Fig. 1: MSP morphology of PNIPAM–PS block copolymer particles prepared with a) ethanol, and b) 1-pentanol as reductant.

Each MSP has a size of up to few micrometers (1–4 µm) and contains few hundred polystyrene (PS) particles with a diameter smaller than 100 nm which are evenly dispersed in a PNIPAM matrix. It is to emphasize that the numerical data refer to the visible particles in the 2D projection of the electron microscopic images and these quantitative data hold for the particular clusters under consideration but nevertheless, these values illustrate the generally observed trend. The MSP formation is not restricted to styrene as second stage monomer **[2]**.

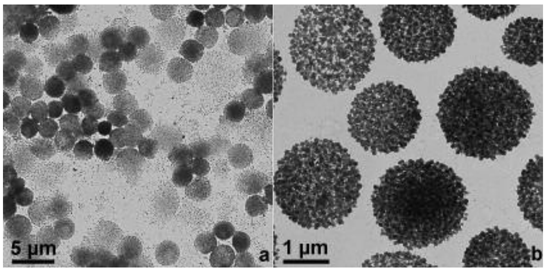

Fig. 2: MSP morphology of a) PNIPAM–PBMA with complex of PEG in α-CD and b) PNIPAM–PVAc–PS block copolymers with β-CD as reductant.

The MSP morphology also has been observed for other monomers such as butyl acrylate (BA), butyl methacrylate (BMA) **(Fig. 2)**, and vinyl acetate (VAc). The lower film formation temperature of poly-VAc, poly-BMA, and poly-BA causes the indistinct appearance of these particles. Sequential addition of VAc and styrene leads to triblock copolymer MSP (PNIPAM–PVAc–PS). PS is the outermost layer and prevents film formation of the nanoparticles **(Fig. 2 b)**.

The morphology of the block copolymer particles generated via redox-initiated aqueous heterophase polymerization with NIPAM depends on the nature of the reductant **[2]**. Using α-CD as reductant leads to stable MSP too. The polymer aggregates are a physically cross-linked and the size of the aggregates is smaller than 4 µm.

Not only in polymer synthesis but also in inorganic aqueous dispersions the stability of colloidal metal oxide nanoparticles is of our research interest.

In combination of dynamic light scattering and transmission electron microscopy the aggregation behavior of hematite and hematite-akageneite composite nanoparticles stabilized with alkyl sulfates was studied in dependence of the pH in the range of 3–11 **[3]**. The iron oxide nanoparticles were dispersed in an ultrasonic batch at solid-to-liquid ratio of 1:5000 by mass in aqueous solutions.

Whereas the ζ potential decreases continuously from lower to higher pH-values, the size of the aggregated particles shows a maximum at the isoelectric point (IEP). The maximum in the level of aggregation matches the minimum in the stability condition of the dispersion.

Typical primary nanoparticles in hematite dispersions are nearly spherical and are 20–80 nm in diameter **(Fig. 3a)**. Most of the particles are in the range 40–70 nm in diameter, and the fraction of particles smaller than 40 nm or larger than 70 nm is low.

Primary particles in hematite-akageneite composite dispersions show two different shapes. On the one hand we found nearly spherical particles similar in shape to those presented in **Fig. 3a,** but considerably larger (80–120 nm in diameter). On the other hand we found lath-shaped akageneite particles of about 100 nm wide and 400–500 nm long **(Fig. 3b)**.

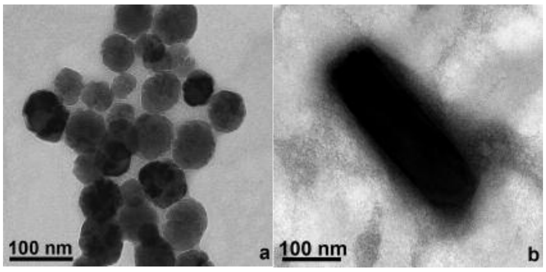

Fig. 3: Primary hematite nanoparticles a),and primary lath-shaped akageneite particle b)

In dispersions of hematite stabilized with C12, C14 and C16 (concentrations in the range 0.1–1 mM) the mean particle diameter of aggregates are pH-independent **[3]**. Typical hematite aggregates are presented in **Fig. 4a.** The dispersion contains different structures, which consists of smaller and bigger aggregates of primary particles, as well as single primary particles. In hematite-akageneite composite dispersions practically all primary particles are aggregated. Even relatively small aggregates contained both lath-shaped particles and spherical particles as illustrated in **Fig. 4b.**

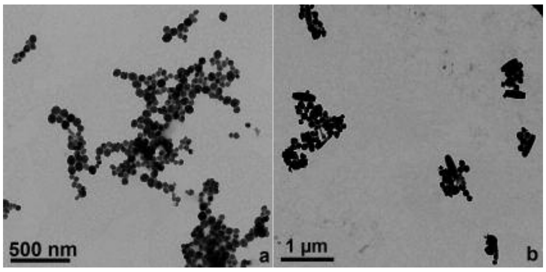

Fig. 4: Aggregates: (a) in dispersion of hematite in 0.1 mM sodium hexadecyl sulfate, pH 9.5, ζ-potential -54 mV; (b) in dispersion of hematite-akageneite composite in 0.1 mM sodium hexadecyl sulfate, pH 4.28, ζ-potential -61 mV.

Apparently heteroaggregation involving both spherical and lath-shaped particles in hematite-akageneite dispersions is preferred over homoaggregation.

All of the electron microscopic investigations confirm the presence of aggregates in dispersions of iron oxides stabilized with alkyl sulfates originally found by light scattering. These are the first experimental results, which directly shows formation of mixed aggregates in dispersions composed of particles having similar chemical compositions (iron oxides), and different morphologies.

Both the colloidal stability and the interfacial morphology of oil/water (O/W) Pickering emulsions play an important role within the development of functional micro- and nanocontainers.

The application of the Layer-by-Layer assembly approach for Pickering emulsions not only stabilizes the emulsion particles, but also closes the interstitial pores of the emulsion nanoparticulated shell thus providing its controlled permeability and release of the materials dissolved in the oil core.

Here, the weak polyacid poly(methacrylic acid sodium salt) (PMAA, Mw~9500g/Mol) and the polybase poly(allylamine hydrochloride) (PAH, Mw~17000g/Mol) were selected for the surface modification of oppositely charged alumina (Al_2O_3) and silica (SiO_2) nanoparticles. The size of the stabile core/shell dodecane/water emulsions droplets are in the range of 500 nm to 2 µm.

There are different shell morphologies of oil/water/silica and oil/water/alumina emulsion droplets in dependence of the chemical surface modification of the silica nanoparticles with PAH and the alumina nanoparticles with PMAA.

The narrow distributed silica nanoparticles with a mean diameter of about 20 nm covers the oil phase by a closed packed mono layer (pH=8.5) **[4]**, whereas the alumina nanoparticles with a mean diameter of about 4 nm form a dense and complete layer of a thickness of about 30 nm (pH=5) consists of aggregates of alumina nanoparticles **(Fig. 5)**.

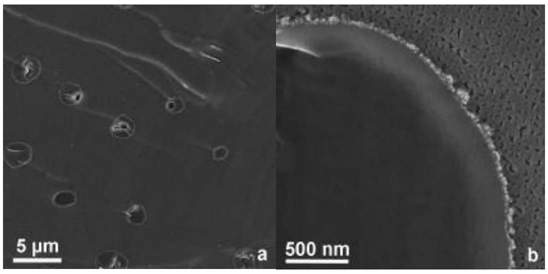

Fig. 5: Dodecane emulsion droplets stabilized with surface modified alumina nanoparticles (a,b)

Above pH > 9, flocculation of silica nanoparticles takes place **[5],** consequentially, the dodecane droplet shell consists almost entirely of particle aggregates. The know-how acquired during development of particle stabilized nano- and microcontainers is applied for encapsulation of different active chemical and biological components.

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Materials for Photo and Electrochemical Reactions

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One of the promising technologies for future alternative energy sources is the direct conversion of sunlight into chemical and electrical energy by using photocatalysis or photoelectrochemical cells (PEC), respectively **[1]**. The greatest challenge in these fields is to develop new types of advanced materials with the desired electrical and optical properties that will replace the conventional raw materials that are currently used. Photocatalysis has attracted great interest over the last decades, especially for its potential to produce clean and cheap renewable energy without dependence on fossil fuels and without carbon dioxide emission. Photocatalysis applications span from many fields such as: solar fuel production, water splitting, photo-degradation of pollutants, and catalysis of other chemical reactions, e.g. for the production of fine chemicals. The photocatalytic operation usually involves photoactive semiconductors, mostly the ones which consist of metal-based semiconductors like TiO_2, ZnO, Fe_2O_3, and many more. For efficient photocatalysis, the internal recombination rate of the charge carriers should be sufficiently low to allow electron/hole migration to the surface of the catalyst, in order to perform the desired reaction. In this system, the photocatalyst is dispersed within the desired solution, and under illumination the charges transfer to the solution and start the desired reaction **(Fig. 1)**.

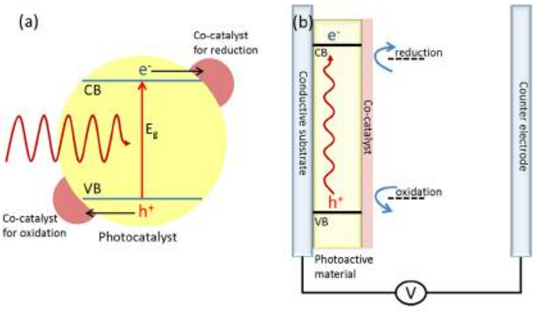

Fig. 1: Illustration of two photocatalysis systems.

The second system is based on photo electrochemical cell (PEC) which is based on semiconductor-liquid junctions which can be relatively efficient with respect to the first system, due to improvement of charge separation under illumination. The PECs can be used in order to convert the solar radiation into chemical energy (i.e. water splitting) or to electric energy (i.e. solar cells). Typically for efficient photo (electro) catalysis, an additional co-catalyst, which is currently mostly based on noble metals, is needed in order to increase the wanted reaction activity and rate. Although in the last years a significant progress has been made in this field, it is still an essential task to find efficient and low cost materials as photoactive materials and co-catalysts. More importantly, it is necessary to gain a basic understanding of the physical properties and the fundamental operation mechanisms in this field.

Metal Free Carbon Nitride-Based Materials

While most of the research in this field is focused on metal based semiconductors (metal oxides, sulfides and nitrides) as photocatalysts, in the last years metal-free graphitic carbon nitride (C3N4) materials have attracted widespread attention due to their outstanding (electro)catalytic and photocatalytic activity.

Despite of the great progress in C_3N_4 synthesis, it is still a standard problem of C_3N_4 chemistry that only rather disorganized textures with small grain sizes are obtained. Therefore, it is essential to find new and simple synthetic pathways to form highly ordered structures of carbon nitride with controlled electronic, optical and catalytic properties.

Recently, this group used the supramolecular chemistry approach to synthesize well-defined structures of C_3N_4 such as hollow boxes, spheres and spherical macroscopic assemblies **[2-4]** with the possibility to control their photophysical and photocatalytic properties **(Fig. 2)**. Supramolecular chemistry provides a great opportunity for the synthesis of nanostructured materials without any further templating techniques. The supramolecular approach includes the use of non-covalent interactions such as hydrogen bonding to form order between building blocks for the desired synthesis. Hydrogen bonds are very useful for controlling molecular self-assembly thanks to the reversibility, specificity, and directionality of this class of interactions. The structure of the final products can be controlled by choosing the appropriate monomers and solvents for the synthesis. The starting monomers will organize into different structures according to their ability to form hydrogen bonds in the given solvent and form ordered and stable aggregates which consecutively define the resulting materials.

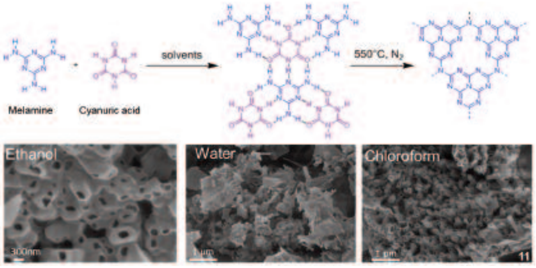

Fig. 2: A graphic presentation of hydrogen-bonded supramolecular complex and the resulting carbon nitride materials in different solvents.

However, for photoelectrochemical applications a direct connection between C_3N_4 and the conductive substrates is needed. Due to the large particle size and the insolubility of C_3N_4 in most solvents, the use of common deposition techniques such as spin-coating and screen-printing results in poor coverage and conductivity. Therefore it is essential to find a new and simple synthetic pathway to grow C_3N_4 on different substrates. Using the supramolecular approach we were able to grow highly ordered carbon nitride structures on different substrates both in solid state and liquid-based growth **[5-6]**.

Thanks to the new deposition methods we were able to show, for the first time, the reduction of water to hydrogen using a metal-free C_3N_4 electrocatalyst. Moreover, we found that the C_3N_4 can act as an absorber and electron accepting layer in polymer solar cell which exhibits a remarkable open circuit voltage of 1 V.

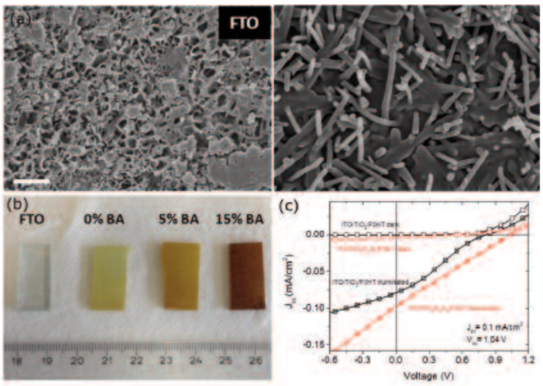

Fig. 3: (a) SEM images of carbon nitride deposited on FTO and glass. (b) Photograph of bare FTO and FTO with C_3N_4 films modified by different amounts of carbon. (c) J-V curves of TiO_2/C_3N_4/P3HT and TiO_2/P3HT solar cells measured in darkness and under 100 mW/cm^2 AM 1.5G illumination.

Carbon Nitride Based Hydrogels

In our lab we synthesize carbon nitride hydrogel with good mechanical properties, high selective pollutants adsorption capacity and photodegradation. Moreover, carbon nitride hydrogel show very promising activity as photocatalyst for the water splitting applications. The synthesis of the carbon nitride hydrogel, with adjustable shape, i.e. cylindrical and tube-like, is acquired through photo-polymerization of poly(N,N-dimethylacrylamide) (DMA) in the presence of well-dispersed highly photoactive carbon nitride as initiator in aqueous solution. In our current research we synthesize new carbon nitride hydrogels toward their utilization as catalysts for various reactions.

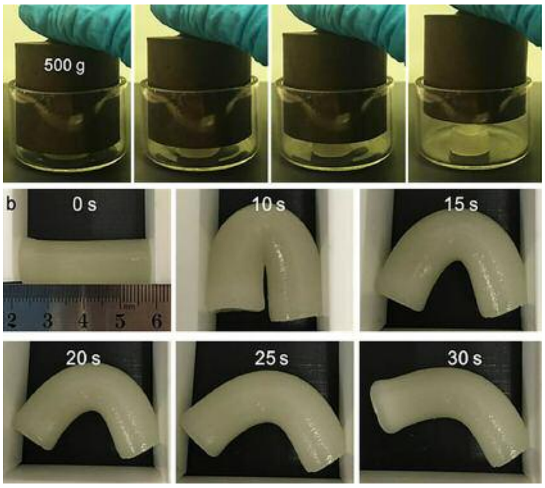

Fig. 4: Carbon nitride based hydrogel.

Ceramic Metals as Water Splitting Electrocatalysts

An important topic of our group is the development of new, low cost and efficient materials as electro and co-catalysts for energy related applications (i.e. water splitting). Electrochemical water splitting to hydrogen (HER) and oxygen (OER) plays a growing role in the fabrication of alternative energy devices due to the need of clean and sustainable energy. Nickel-based materials have attracted enormous attention because of the flexible catalytic properties, along with low price and high abundance when compared to noble metals.

We developed a facile and easy synthesis of large- scale nanoporous, nickel based materials (Ni, Ni_5P_4, Ni_3N and Ni_3S_2), partly embedded in an amorphous matrix of a carbon-nitrogen material or directly grown on Ni substrates. The obtained materials show remarkable performance in the electrochemical production of hydrogen and oxygen both in terms of low overpotential and high current densities. In sum, the activity of these materials results in a high overall water splitting efficiency.

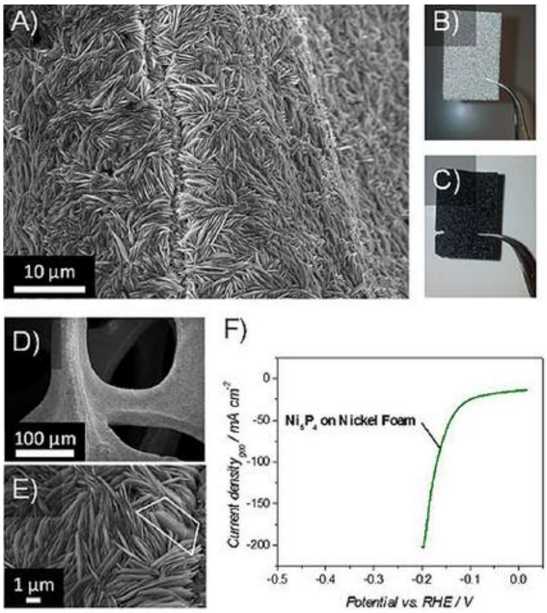

Fig. 5 (a) SEM image of Ni_5P_4 on Ni foam (b) picture of Ni foam and (c) modified Ni_5P_4/Ni foam and the corresponding SEM image of (D-E) the modified foam. (f) Linear sweep voltammetry of Ni_5P_4/Ni foam which shows the hydrogen evolution reaction activity.

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Polymer Dispersions / Heterophase Polymerizations

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Heterophase polymerization (HP) is a centennial technology and the base for producing a great variety of polymer dispersions in both laboratory and industrial scale. Better understanding of the basics of HP and educating students on this topic is of general scientific and economic interest and a goal in the very core of the activities of our research. Amongst others the following results have been published 2015-16.

Swelling of Latex Particles and the Role of Monomer Drops during Heterophase Polymerization

The role of monomer drops went unnoticed for many decades. It is state of the art to consider the monomer drops play an only passive role as storehouse for the monomer since the 1940-ies of the last century. Accordingly, the monomer molecules enter the polymer particles from the drops via diffusion through the aqueous phase. However, these state of the art concepts are challenged by new experimental and simulation results **[1, 2]**. Taking advantage of an experimental method which was previously developed in our group **[3]** we were able to prove that fast swelling of polymer samples cannot occur via diffusion of individual molecules of the swelling agent through the aqueous phase but requires direct contact with drops of the swelling agent **(Fig. 1)**.

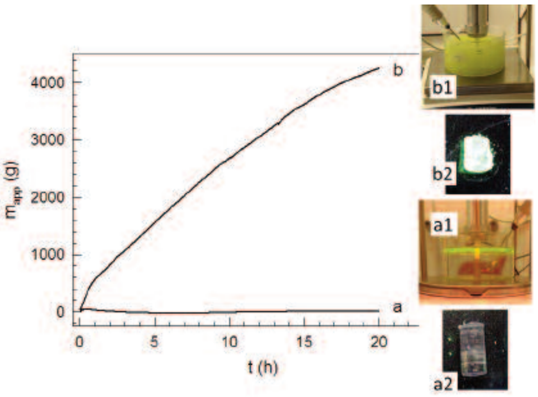


Fig. 1: Influence of the stirring rate on the swelling of crosslinked polystyrene with ethyl benzene labeled with water-insoluble fluorescence dye; the graph shows the temporal development of the swelling pressure (expressed as apparent mass, m_{app}); curve a – unstirred (only diffusion, image a1), b – vigorous stirring (drop formation and advection, image b1); fluorescence of the polymer sample (image b2) proves successful swelling in contrast to image a2

The conclusions drawn from these non-polymerization experiments for the conditions during HP are impossible directly to prove in polymerization experiments. However, simulation results using Fick's laws support the necessity of direct contact between monomer droplets and latex particles for a sufficiently high monomer concentration inside the particles as observed during emulsion polymerization **(Fig. 2) [4]**. For monomer concentration $C_{M,P} \geq 2.6$ M which is in accordance with Fick's law also necessary at the particle – water interface, the monomer diffusion is faster than propagation ($f^2_{Th} < 1$) and equilibrium swelling is maintained. If however, $C_{M,P} < 2.6$ M the replenishment of monomer via diffusion is not fast enough and the particle, with respect to monomer, starves out.

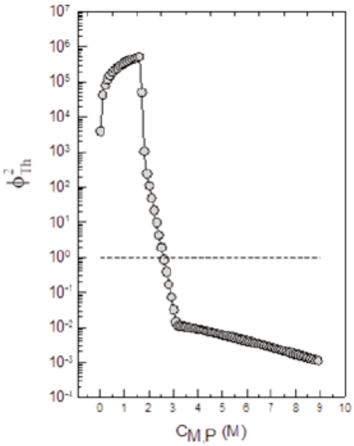
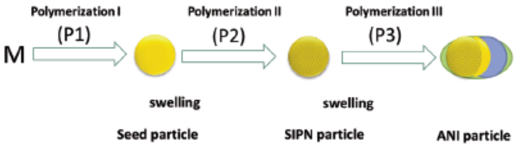


Fig.2 Correlation of the Thiele modulus (f_{Th}) with the monomer concentration inside a 100 nm particle ($C_{M,P}$) containing one polymerizing radical; the calculation was made with assuming an equilibrium situation with respect to $C_{M,P}$ at the particle interface and inside

$$\Phi^2_{Th} = \frac{k_P C_{M,P} \cdot r_0^2}{\tilde{D}}$$

Swelling-Induced Formation of Anisotropic Latex Particles

The mass production of non-spherical latex particles directly via aqueous heterophase polymerization is quite a tedious process **(Fig. 3)** and requires more than one subsequent polymerization step, typically three with additionally repeated purification stages in between **[5]**.



Fig, 3 Illustration of the procedure for the synthesis of anisotropic particles via the direct polymerization route comprising three consecutive polymerizations (P1 – P3) and two swelling steps; typically but not necessarily the monomers for P1 and P2 are the same, however, P2 is carried out in the presence of a crosslinker and leads to the formation of a semi-interpenetrating network (SIPN), and for P3 a different monomer can be chosen; the different colors sketched in the anisotropic particles represent different polymers assumed to be in the final particles; yellow – SIPN portion, blue – portion of the polymer generated during P3, green – mixed portion of polymer (mainly due to chain transfer to polymer)

In addition, the last polymerization step requires SIPN particles. The experiments described so far in the public scientific literature seemingly are in agreement with the mechanistic idea based on elastic network relaxation by increasing temperature.

Here we communicate experimental results proving that the swelling of SIPN seed particles is the crucial step for the synthesis of anisotropic polymer particles via seeded heterophase polymerization but not the increase of temperature **(Figure 4) [5]**.

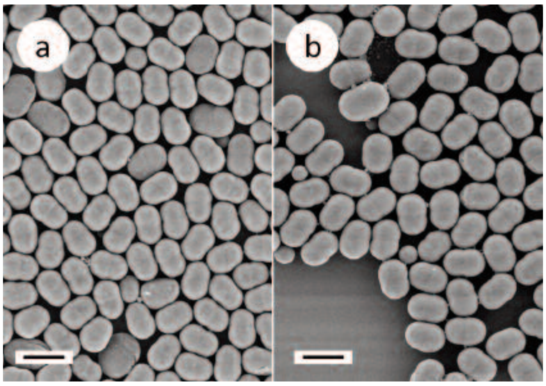


Fig. 4. SEM micrographs of anisotropic particles obtained with V65 at 70 °C (image a) and with Irgacure® 819 at room temperature (image b); styrene as monomer during P1 and P2, methyl methacrylate as monomer during P3; scale bar 2 µm

The isothermal deformation of micrometer-sized spherical SIPN particles due to swelling can be directly observed with light microscopy **Figure 5**). The degree of deformation depends on both the time after addition of the swelling agent and the distance of the particles from the swelling agent – water interface.

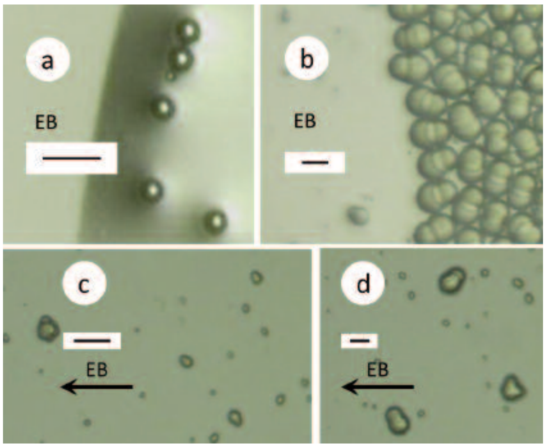


Fig. 5. Optical micrographs illustrating the development of polystyrene-SIPN particles' morphology during swelling with ethyl benzene (EB) over time; a – before, b – 12.5 h, c – 12 min, and d – 44 min after the addition of EB to the cuvette

The experimental data show that the direct formation of anisotropic colloidal polymer particles via aqueous heterophase polymerization is essentially controlled by the entropy gain of the linear fraction in the semi-interpenetrating network of the seed particles during swelling. This conclusion is supported by simulation results with a thermodynamic model. The larger compartment of the anisotropic particles contains the linear polymer chains and exhibits a volume-based swelling ratio of about 130 compared to about 7 of the smaller section containing the crosslinked polymer fraction.

Ionic Liquids Can be Used to Make Durable Wood Connections

The weighing method as described recently **[3]** is an easy to use and versatile tool to study also the swelling behavior of wood. The measuring system is open and hence, during the measurements the composition of the swelling agent can be changed without interrupting the data recording. This feature allows transient measurements, i.e. following uptake and release of volatile swelling agents. Studying the swelling of wood samples with a mixture of ionic liquids and water revealed a particular behavior **[6]**. On the one hand water swells wood much faster and stronger than the ionic liquid alone and on the other hand it facilitates the uptake of the ionic liquid. Transient studies have shown that water evaporates alone but the ionic liquid remains in the wood causing a sustained swelling. The durable swelling with the ionic liquid is useful for the construction of permanent joints in wood-containing assemblies. To detach the beech cylinder from the aluminum ring **(cf. Fig. 6)** requires 270 N. Another benefit for the application of wooden construction can be expected with respect to antifouling and antibacterial protection because it is known that ionic liquids are effective in this sense.

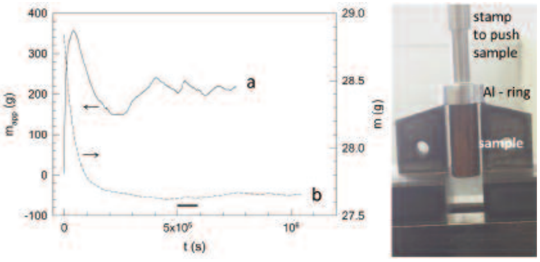


*Fig. 6. **Graph:** following the swelling of a cube of spruce wood (edge length 20 mm) with water (1.1 g) added 4 days after the addition of ionic liquid (1-hexyl-3-methylimidazolium chloride) (m_{app}, solid line a, left y-axis) and the weight loss (m, dashed line b, right y-axis); the short solid line parallel to the x-axis represents 24 hours; **Image:** beech wood cylinder (outer diameter in dry state of 8 mm) connected to an Al ring (inner diameter of 8.3 mm) by swelling with ionic liquid (ethylammonium nitrate) prepared for measuring the force to detach*

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POLY(IONIC LIQUID)S: SYNTHESIS AND MATERIALS APPLICATION

Poly(ionic liquid)s as a Multifunctional Materials Platform

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Poly(ionic liquid)s (PILs) are polymers produced *via* polymerization of monomeric ionic liquids (ILs).**[1]** The marriage between ILs and polymers combines synergistically some unique properties of ILs with the general processable and mechanically stable profile of polymers. Thus PILs possess an unusually broad spectrum of properties and functions that attract tremendous interest in the fields of polymer and materials science. The aim of the current study on PILs is generally to understand their fundamental physics and chemistry, as well to realize their numerous materials applications, which are preferentially energy and environment-oriented. Our group is pioneering the PILs research, and devotes itself to discovering new science and practical usage of PILs in membrane technology **[2-3]**, colloidal science **[4-5]**, responsive materials **[6-8]**, innovative stabilizers **[9]**, and carbon nanostructures **[10]**.

PILs for Nanoporous Carbon Membranes

Freestanding nanoporous carbon membranes hold great promise in catalysis, water treatment, biofiltration, gas separation and optoelectronics, just to name a few, because of their structural integrity, continuity, and purity. When they are used as an electrode in electrochemical energy conversion/storage or nanoelectronic devices, precise control over key structure parameters and synthetically easy access to membranes of large size and large surface area, is highly relevant but cannot be fully met by the state-of-the-art synthetic protocols. These structure parameters include the atomic order, local chemical composition, nanoscale morphology and complex pore architecture. In this context, the PILs group reported recently a bottom-up approach to fabricate hierarchically structured, nitrogen-doped, graphitic nanoporous carbon membranes (termed HNDCMs) *via* morphology-retaining carbonization of a porous PIL membrane precursor (**Fig. 1a**) at low-pressure under N_2 atmosphere **[2]**. This is a joint project with Professor Tom Wu in the King Abdullah University of Science and Technology (KAUST).

The HNDCMs produced at 1000 °C, are conductive (200 S/cm at 298 K), N-doped (5.7 wt%), and graphitic (single-crystal-like). In addition, the HNDCMs bear a hierarchical porous structure with two sets of pores: a set of large pores of 30nm - 2µm (pore set I) and a set of small pores of < 30 nm (pore set II). A unique feature of the HNDCMs is the presence of a pore size gradient of pore set I across the membranes, with large pores on the top and small ones at the bottom (Fig. 1B-1E). Gradient property in materials science is exotic and useful to tailor materials property, where high-energy interfaces in multicomponent systems can be avoided. Gradient property is a core difference between HNDCMs and powderous carbons, as well as common porous carbon membranes. The HNDCMs are appealing as binder-free electrodes to be used in electrochemical energy devices due to the high electron conductivity, catalytically active sites stemming from nitrogen-doping, and hierarchical pore architecture. As a proof-of-concept, Co nanoparticles could be loaded in these membranes and served as high performance electrocatalyst for H_2 evolution in alkaline condition at low overpotential. In the future, HNDCMs might have the potential to be further used to replace the powderous carbon electrodes in many other electrochemical energy devices, such as batteries and fuel cells, to improve long-term electrochemical stability.

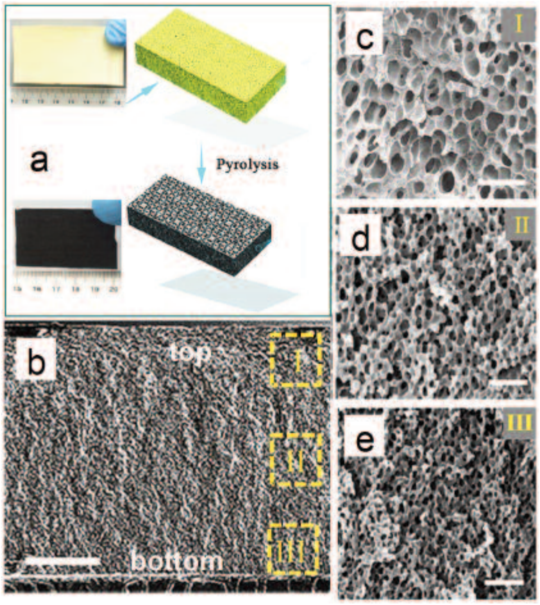

Fig. 1: a) Synthetic scheme towards nanoporous N-doped gradient carbon membranes. The paragraphs on the left are a freestanding porous PIL membrane before (top, 7.2 x 3.3 cm^2) and after carbonization (bottom, 5.2 x 2.5 cm^2). b) SEM cross-sectional view of the carbon membrane. Scale bar 20 µm. c-e) Enlarged SEM images of the local cross-sectional areas (boxes I, II and III). Scale bar: 500 nm.

PIL ellipsoid-like Nanoparticles

Both the surface and the inner morphology of polymer nanostructures are crucial to define their properties and functions, and require precise control. Versatile techniques and methods have been devoted to this endeavor, which are dominated by manipulation of their shapes, surface functionalities or dimensions, leaving their interior rarely addressed. The capability to tailor not only the overall shape but also fine interior represents a high-level of control over characteristics of polymer (nano)particles that is inevitably required for task-specific functions and applications. When particles are downsized to <50 nm, *i.e.* approaching the size of some individual polymer chains, suitable synthetic approaches or fabrication techniques are missing in polymer science. This piece of knowledge is now harvested in our investigation of 1,2,4-triazolium PIL nanoparticles, which is a joint project with the Schmidt group in the Colloidal Chemistry department **[4]**. In these extremely small nanoparticles (below 50 nm and bearing sub-5 nm domain size), we identified and analyzed an unusually striped ellipsoid-like morphology **(Fig. 2)**. The chemical structure of the PIL is shown on the left in **Figure 2**, which contains a long hydrophobic dodecyl alkyl chain and a hydrophilic ionic backbone. In the cryogenic transmission electron microscopy (Cryo-TEM) image **(middle in Fig. 2)**, the dark lamellae represent the PIL backbone because of the high electron density of bromide anions, while the gray zones are from the alkyl chain domain. The ellipsoid- instead of onion-like morphology is a balance of the surface energy among the hydrophobic dodecyl domain, the hydrophilic backbone domains, and the surround water. The ellipsoid-like nanoparticles are structurally complex and well ordered, yet synthetically easy-to-make in a one-pot dispersion polymerization process.

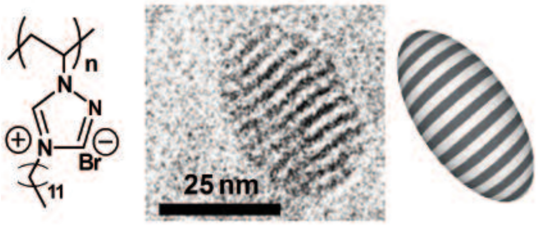

Fig. 2: Left: chemical structure of the 1,2,4-triazolium PIL nanoparticles. Middle: Cryo-TEM image of a single ellipsoid-like PIL nanoparticle. Right: a cartoon illustration of the PIL nanoparticle.

PILs as Innovative Stabilizers

The creation of inorganic materials with tailored structures and morphologies has continued advancing materials chemistry by offering new properties and applications. Previous synthesis using polymers as stabilizers and crystal growth modifiers has achieved substantial success in making systems with targeted properties. In PILs, the structural synergy coupling with their good solubility in organic solvents can create newly structured materials, which has remained unexplored. Our latest progress demonstrated PILs as additives for the morphogenesis of transition metal chalcogenides **[9]**, here exemplified by a highly photoconductive semiconductor, bismuth sulfide (Bi_2S_3) with a direct band gap (Eg) of ~1.3 eV. Current approaches for making Bi_2S_3 described overwhelmingly one-dimensional (1D) structures, because of its highly anisotropic crystal structure consisting of infinite chains of covalently bound atoms. When PILs were used, we could modify the nucleation and growth of Bi_2S_3 materials in organic solvents, which leads to unique crystals with highly tailored sizes, dimensions and architectures, and in consequence a tuneable Eg owing to the quantum-size effect.

As shown in **Fig. 3,** commercially available or readily synthesized PILs, including poly(1-methyl-3-(4-vinylbenzyl)-imidazolium chloride) (PIL-1), poly(diallyldimethylammonium bis(trifuoromethane sulfonyl)imide) (PIL-2), and poly(3-ethyl-1-vinyl-imidazolium bromide) (PIL-3), are applied as exemplary additives. All these PILs are soluble in N,N-dimethylformamide (DMF), a polar organic solvent used here. The syntheses were performed in a simple solvothermal system, composing of mixtures of DMF, $Bi(NO_3)_3$, CH_4N_2S and PILs in appropriate ratios, which were then heated at desired temperature to induce crystallization **(Fig. 3)**. Notably, the three PIL additives resulted in significant morphological diversity of the achieved materials, owing to their different cations, anions, and backbone architectures that selectively couple with specific crystal faces, to modulate and even template consecutive growth, strongly evidencing the effective role of PILs in modifying the crystal growth pattern.

A broad set of characterization techniques confirms that the participation of PILs in the synthesis of Bi_2S_3 can not only control the synthesis, but also enable surface electronic structure modulation, endowing the resultant Bi_2S_3 with enhanced catalytic performance. This was illustrated by an important but notoriously difficult reaction, *i.e.* the anodic water oxidation reaction of water electrolyzers, where it can compete with the reference RuO_2 catalyst, while its commercial counterpart is almost catalytically inactive.

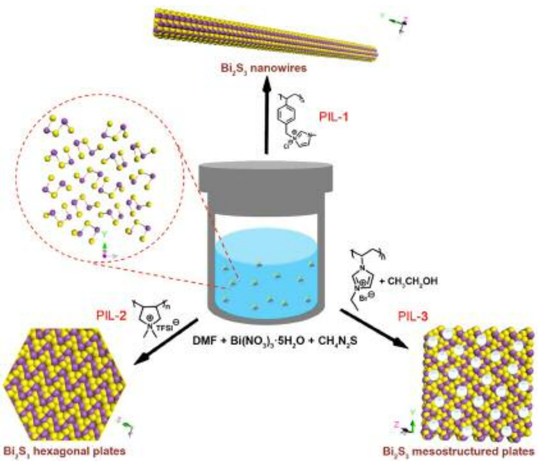

Fig. 3: Schematic illustration of the PIL-controlled synthesis of Bi_2S_3 crystals. High-quality Bi_2S_3 crystals with significant morphological diversity are created by using various PILs as synthetic additives. Inset in red dotted circle shows the crystal structure of Bi_2S_3 projected on the (001) plane. Purple and yellow balls indicate Bi and S atoms, respectively.

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SUSTAINABLE ENERGY STORAGE MATERIALS

Using Polymers and Ionic Liquids for Next Generation Energy Storage Devices

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Lithium ion batteries are ubiquitous in today's society due to their high energy density and rechargeability. Applications which require less energy often utilize cheaper batteries based on zinc, cadmium, lead, or nickel. All of them however pose dangers regarding flammability, corrosivity, or toxicity of electrodes or electrolytes if handled incorrectly or malfunctioning. Reports of burning laptops and cell phones (usually caused by malfunctioning lithium ion batteries) or skin burns and deformities (often caused by exposure to heavy metals or battery acids) are reoccurring on a regular basis. Apart from their dangers, metals as currently employed in batteries have a significant negative environmental impact during mining (since many of them are rare) or insufficient recycling.

For next generation energy storage devices, other metals like magnesium or aluminium might be a safe alternative since even in their elemental form they will not overheat or catch fire when exposed to humidity, in contrast to lithium. The environmental impact is also lower since there is 1000 times as much of these metals in the earth crust compared to lithium. Because of their multivalency, ion radius, and, especially in case of magnesium, electrochemical potential, batteries based on such metals will still have higher energy densities when compared to current lithium batteries. Reactivity and fast passivation however currently hinder widespread application, and prototypes only work in combination with selective electrolyte compositions. One approach in our group is to develop ionic liquid electrolytes to be used in future magnesium batteries. In addition to their electrochemical stability, such electrolytes will decrease the risk of explosion of electrical devices since they are not volatile.

Another approach to reduce the environmental impact of energy storage devices is to use organic molecules as electrodes instead of metals or metal oxides. Polymers with redox functionalities are especially interesting since they are more difficult to dissolve in electrolytes, and charge transport between active groups is facilitated compared to low molecular species. Both natural and synthetic polymers may be used, and disposure is much more benign since incineration of waste electrodes after usage will prevent hazardous refuse while not producing more dangerous gases then when incinerating other plastics. We research the possibilities of using synthetic and natural polymers as electrode material in batteries and supercapacitors.

Sustainable Ionic Liquid Electrolytes for Battery Applications

Ionic liquids are considered a safe and electrochemically stable alternative to chemical solvents and may find applications in a multitude of fields, amongst others in battery electrolytes. By introducing functional groups, a plethora of so-called task-specific ionic liquids is available. For applications in electrochemistry, amongst others a large electrochemical stability range and liquidity at low temperatures are desirable. Applications which involve ionic liquids often comply with green chemical principles such as waste prevention, benign reaction conditions, reduced toxicity, efficiency, and minimized hazard and accident risk. In most cases, however, synthesis of ionic liquids is neither "green" nor cheap since usual reaction routes include expensive and harmful chemicals like alkyl halides.

We used the modified Debus-Radziszewski reaction and reagents which are potentially derived from renewable resources to synthesize task-specific ionic liquids for applications as possible electrolyte in magnesium batteries. By introducing tetrahydrofurfuryl side groups, we may exchange the common solvent in prototype magnesium batteries, THF, by a safe, non-volatile, non-flammable, and electrochemically stable alternative, gained from cheap and potentially renewable resources. Reaction conditions were benign, and the products exhibited a large range of liquidity and electrochemical stability (**Fig. 1**) **[1].**

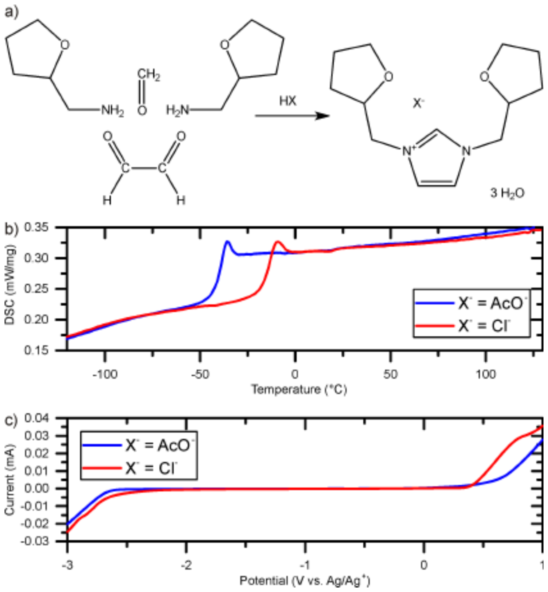

Fig. 1: (a) Schematics of the modified Debus-Radziszewski reaction yielding substituted imidazolium ionics in a simple one-step reaction without using alkyl halides. (b) DSC thermogram demonstrating low glass transition temperatures (well below 0 °C) of the imidazolium products shown in (a) with different counter ions. (c) Linear sweep voltammograms of the imidazolium ionic liquids. The sample with Cl^- counter ion can also be obtained by metathesis of the sample with AcO^- counter ion; the graphs in (b) and (c) derive from a product obtained by metathesis ***[1].***

Redox Active Polymers as Electrode Material

To reduce cost, hazards, and environmental impact, electrode materials in future energy storage systems might derive from organic molecules with redox functionalities. Easy and large-scale synthesis, a suitable electrochemical potential of the redox reaction, and reversibility of oxidation/reduction are some of the most important properties. To prevent dissolution in the electrolyte, polymers with pendant redox active groups may be advantageous, and blending the polymers with high surface area carbon leads to synergistic double layer capacitance with redox processes. Binders like fluorinated polymers also help preventing dissolution.

Redox functionalities may derive from, e.g., nitroxyl radicals or quinones. Synthetic polymers have the advantage that functionalized units are defined and can be adjusted. Mixing in other polymers to include different tasks like conductivity or non-solubility and patterning surfaces with redox functionalities is possible by synthesizing block copolymers. **Fig. 2** shows the surface structure and corresponding cyclic voltammogram of a synthetic block copolymer featuring one redox active nitroxyl containing block and a polystyrene block **[2].**

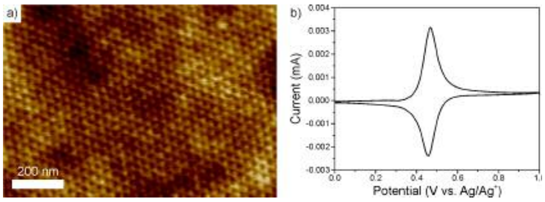

Fig. 2: (a) AFM topography image of a polystyrene-block-poly(2,2,6,6-tetramethyl-piperidinyloxy-4-yl methacrylate) block copolymer synthesized by anionic polymerization featuring a majority block with stable nitroxyl radicals. The AFM image after solvent vapor annealing on a patterned surface shows upright-standing polystyrene cylinders in a matrix which contains redox active stable radical groups. (b) Cyclic voltammogram showing the reversible redox activity of this block copolymer ***[2].***

Ordered structures like in **Fig. 2** are possible only because the polymer has a very low dispersity of 1.06. While synthetically this is challenging (here: anionic polymerization), natural monodisperse polymers exist and might be available in large scales. Natural monodisperse polymers with redox active groups, however, do not feature a high density of redox functionalities. In contrast, lignin, which is one of the main constituents of all plant material, is a biopolymer with a high density of redox active hydroquinone functionalities (after demethylation of methyl ethers) but rather polydisperse. We investigated its application as electrode material after blending with high surface area conductive carbon and some binder. Resulting organic electrodes are cheap and environmentally friendly. For charge storage, they combine electric double layer capacitance at the high surface area conductive carbon with redox reactions in the reversible quinone-hydroquinone redox couple (**Fig. 3**) **[3].**

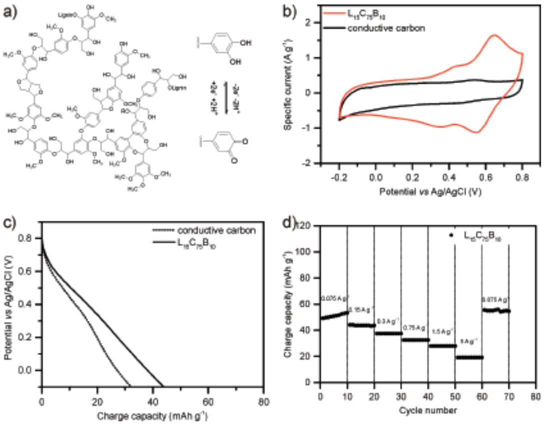

Fig. 3: Electrochemical behaviour of lignin-based organic electrodes. (a) Schematical structure of lignin and the respective redox reaction. (b) Cyclic voltammograms of electrochemical cells with lignin-based working electrode and platinum counter electrode. Compared to carbon electrodes, redox reactions contribute to additional charge storage. (c) Galvanostatic discharge measurements at a current density of 0.15 A g^{-1}. (d) Rate capability by stepwise galvanostatic cycling of the composites from lignin and conductive carbon.

Carbon Nitrides for Photocatalytic Hydrogen Evolution

A different path towards sustainable energy is the photocatalytic production of hydrogen gas to be used in fuel cells. Energy from sunlight is converted to chemical energy which can later be used for powering cars, for example. While conventional catalysts for the hydrogen evolution reaction are often based on platinum, development of suitable carbon nitride catalysts will greatly decrease their costs and contribute to economical and ecologically benign energy storage in form of chemical energy. The morphology and texture of carbon nitride greatly influences performance, and studies of carbon nitride formation are hence crucial for developing highly active materials.

Via supramolecular self-assembly, cyanuric acid-melamine complexes were formed. Sequential treatment with different solvents led to formation of core-shell particles, and calcination resulted, depending on the solvents, in hollow structures and structures with platelet-like surface structure. The formed carbon nitrides showed significantly higher activity for the hydrogen evolution reaction (depending on the morphology up to 10 times as high) compared to bulk carbon nitride **[4].**

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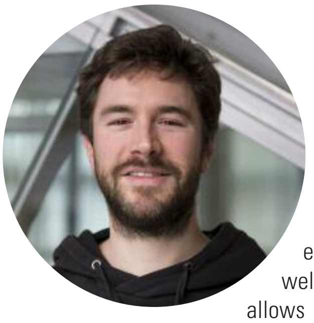
Polymer Synthesis and Self-Assembly for Novel Soft Materials



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Polymers offer a plethora of available structures from the nano- to micrometer range and self-assembled structures from polymers find various applications, e.g. in biomedicine or organic electronics. Moreover, the polymer properties depend to a great extent on polymer microstructure. Therefore, well-controlled synthesis of polymer materials allows for the formation of materials with tailored properties and research on synthetic polymer formation procedures offers the opportunity to generate polymer materials with novel or enhanced properties. Especially, when complex self-assembly processes are targeted, efficient synthetic tools are needed, e.g. reversible deactivation radical polymerization or modular ligation chemistry. In such a way, complex polymer materials can be designed and utilized for self-assemblies that feature specific properties. In this group two topics regarding self-assembly of polymers and synthetic polymerization methodology are investigated. On one hand self-assembly of double hydrophilic block copolymers (DHBCs) in aqueous solution is investigated with the aim to obtain drug-delivery vehicles for complex drugs. On the other hand metal-organic frameworks (MOFs) are utilized as catalysts as well as reaction environment for polymerization reactions.

Double Hydrophilic Block Copolymer Self-Assembly

Unlike the well-known self-assembly of amphiphilic block copolymers, self-assembly of DHBCs in aqueous media is not based on interactions of hydrophobic blocks. Taking a step back looking at water-soluble homopolymers, aqueous biphasic systems can be generated from water-soluble homopolymers, where each homopolymer type is present in one of the aqueous phases. Such a phase separation is possible, when the concentration of the polymers is high enough and significant differences in the hydrophilicity of the homopolymers are present. In the case of a covalent connection of both homopolymers as a block copolymer demixing on the microscopic scale is possible.

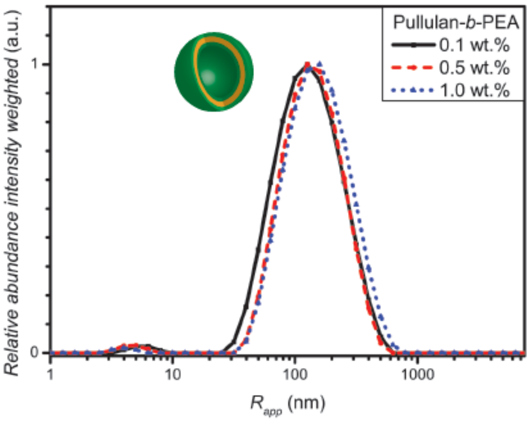

Fig. 1: Self-assembly of pullulan-b-poly(N-ethyl acrylamide) in water observed via DLS at 25 °C ***[1].***

In order to obtain DHBC-based self-assemblies, polymer synthesis has to be performed at first. A suitable tool is reversible deactivation radical polymerization that allows the formation of well-defined polymers, e.g. block copolymers or polymers with specific endgroups. In principle it is possible to form DHBCs from a macroinitiator **[2]** or to conjugate two distinct blocks with specific endgroups.**[1]**

In a subsequent step self-assembly of the formed DHBCs in water can be probed via dynamic light scattering (DLS) (**Fig. 1**), e.g. for the polymer system pullulan-*b*-poly(*N*-ethyl acrylamide).**[1]** Particle size distributions generated from DLS show the formation of particular structures with radii around 200 nm. Moreover, imaging with cryo scanning electron microscopy shows spherical structures that can be attributed to the formation of self-assembled hollow structures (**Fig. 2**).

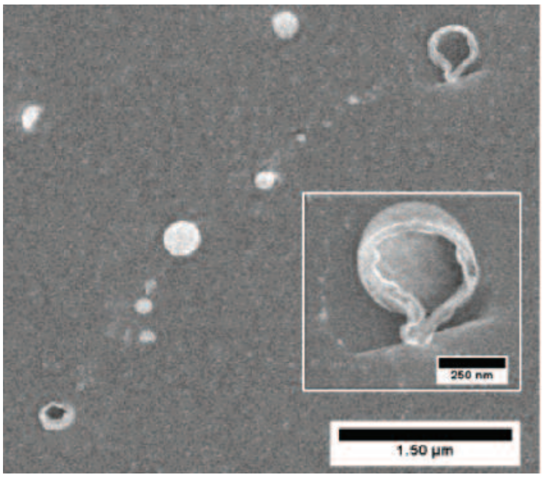

Fig. 2: Self-assembly of pullulan-b-poly(N-ethyl acrylamide) in water: Cryo SEM imaging ***[1].***

One drawback of DHBC-based self-assemblies is their instability in diluted solutions, which poses a significant problem with respect to applications in biomedicine. In order to overcome this problem, a crosslinking strategy was developed. Therefore, the block copolymer poly(ethylene oxide)-*b*-poly(*N*-vinylpyrrolidone-co-*N*-vinyl imidazole) was synthesized.**[2]** The vinylimidazole units allow the formation of crosslinks via nucleophilic substitution reaction with dihalogenide molecules. In such a way the formed particular structures could be preserved even in high dilution and in organic solvents (**Fig. 3**).

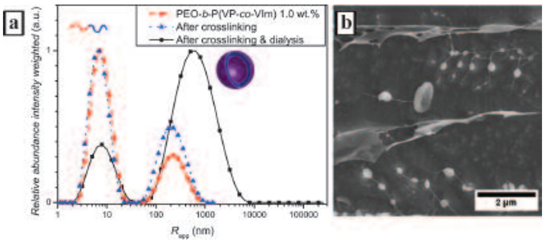

Fig. 3: Self-assembly of poly(ethylene oxide)-b-poly(N-vinylpyrrolidone-co-N-vinyl imidazole) in water: a) DLS at 25 °C before crosslinking at 1.0 wt.%, after crosslinking and at 0.06 wt.% after dialysis, b) cryo SEM of the crosslinked particles ***[2].***

Metal-Organic Frameworks as Polymerization Catalyst and Reaction Environment

MOFs provide porous networks with defined pore sizes and architectures. Moreover, the incorporation of carefully chosen metal ions endows MOFs with catalytic properties.

One of the most frequently used reversible deactivation radical polymerizations is atom transfer radical polymerization (ATRP) that is a Cu(I) catalysed process. More recently activators regenerated by electron transfer (ARGET) ATRP was developed, which is based on Cu(II) reduction to form the catalytic active species. To catalyse polymerizations a Cu(II)-based MOF was formed via complexation of Cu(II) ions, terephthalic acid and 1,4-diazabi-cyclo[2.2.2]octane (DABCO) as a 3D crystalline porous network. In a subsequent step, MOF, monomer, reduction agent (DABCO) and initiator were mixed and heated to start the polymerization. Monomers like styrene, benzyl methacrylate, isoprene and 4-vinylpyridine could be polymerized that way in a controlled fashion as shown via chain extension experiments and narrow molecular mass distributions (**Fig. 4**). More importantly, MOF catalyst could be removed easily via centrifugation and recycled several times.

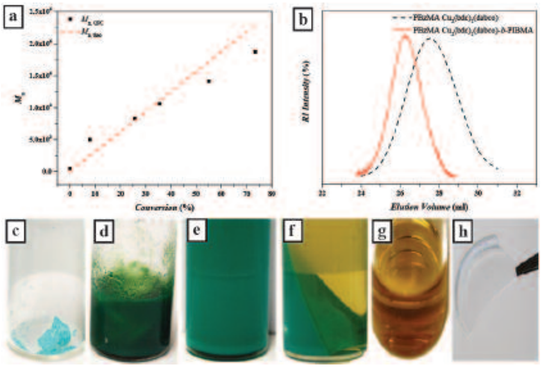

Fig. 4: a) Kinetic plot for the MOF catalyzed polymerization of benzyl methacrylate, b) chain extension, c) MOF catalyst, d) polymerization mixture, e) polymerization mixture after termination, f) centrifugation, g) solution after removal of catalyst and h) final polymer material ***[3].***

After studying the polymerization outside of MOF crystals, polymerization in porous frameworks of MOFs was investigated. The pore diameters of MOFs can be adjusted via utilization of defined precursors in the range of 1–2 nm. Thus, monomer molecules can be introduced into the porous structure that provides a confined environment for the small monomer molecules. That way molecular movement during the polymerization of the monomers is significantly hindered, which should lead to improved stereocontrol/tacticity during polymerization. Again ARGET ATRP was chosen as polymerization technique to conduct polymerizations in controlled fashion. Polymerizations inside of MOFs led to polymers with narrow molecular mass distribution and chain extension proved the controlled character of the polymerizations (**Fig. 5**). Interestingly, studies on the tacticity of the obtained polymers showed a significant effect of monomer size. Methyl methacrylate led to slightly increased isotactic polymer structures compared to the bulk without MOF, while benzyl methacrylate led to significantly increased isotactic fractions (**Fig. 4**). Moreover, the very bulky monomer isobornyl methacrylate did not form any polymer in the MOF as it does not fit into the porous framework. Thus, a significant effect of the confined porous environment on polymer tacticity is indicated.

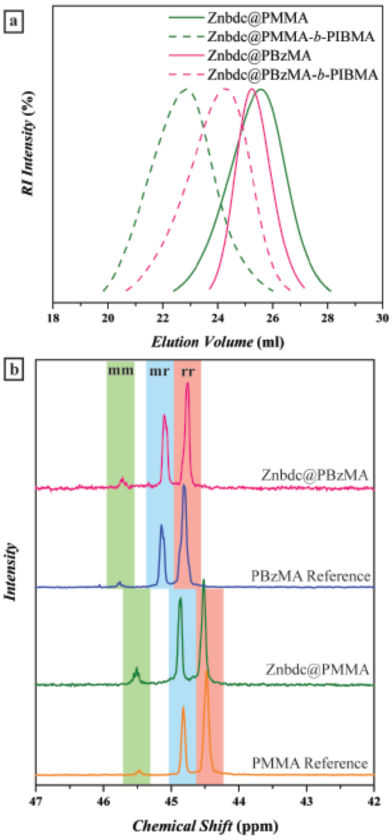

Fig. 5: a) Chain extension of poly(methyl methacrylate) and poly(benzyl methacrylate) obtained via ARGET ATRP in a MOF and b) ^{13}C *NMR spectra of poly(methyl methacrylate) and poly(benzyl methacrylate) obtained via ARGET ATRP in a MOF and the corresponding reference from bulk polymerization* ***[4].***

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[4] Lee, H.-C., Antonietti, M., Schmidt, B.V.K.J.: Metal-Organic-Frameworks as Confined Reaction Environment for Reversible-Deactivation Radical Polymerization. in preparation (2017).