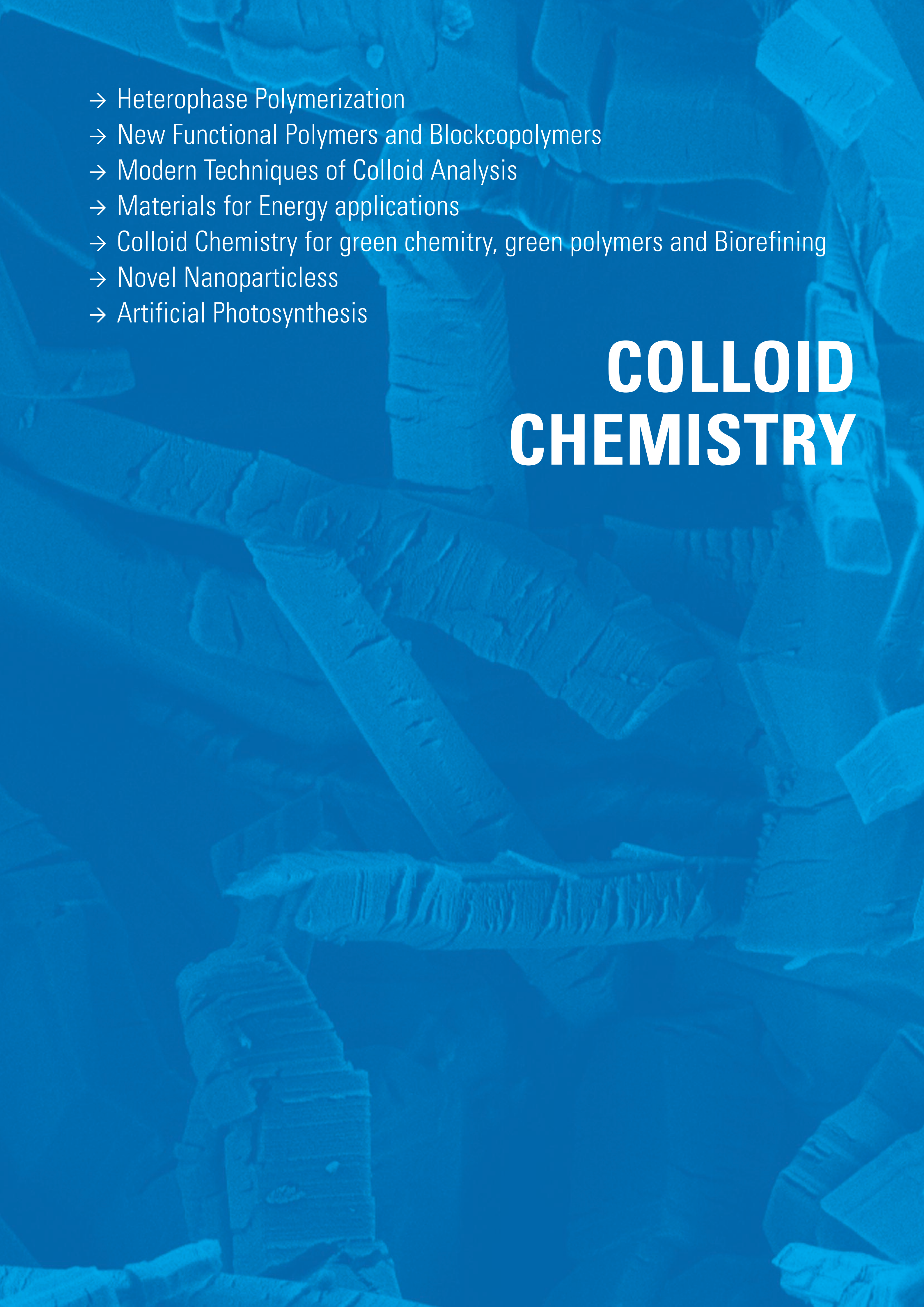

- Heterophase Polymerization
- New Functional Polymers and Blockcopolymers
- Modern Techniques of Colloid Analysis
- Materials for Energy applications
- Colloid Chemistry for green chemitry, green polymers and Biorefining
- Novel Nanoparticless
- Artificial Photosynthesis

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 is currently about 70 people, 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 postdocs (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 two periods continues to take place. Dr. Schlaad, a permanent staff member working with me for 15 years, just left for a Full Professorship of the University of Potsdam, Dr. Jens Weber got promoted to Professor and the Applied University of Görlitz-Zittau. Dr. Filipe Vilela was called for a Senior lecturership to Scotland, while Dr. Cristina Giordano is in the very last phases of completing her Habilitation.

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 idea that result oriented. This turnover of leading junior scientists is beyond typical and easy, but reflects the dynamic character of the department. The profile of the department has therefore continued to be reoriented, keeping only some of the old strongholds.

The following topics are currently explored within the department:

- Heterophase Polymerization
- New Functional Polymers and Blockcopolymers
- Modern Techniques of Colloid Analysis
- Materials for Energy applications
- Colloid Chemistry for green chemitry, green polymers and Biorefining
- Novel Nanoparticless
- Artificial Photosynthesis

The projects behind the headers are briefly explained below:

Heterophase Polymerization

The notation "Heterophase Polymerization" summarizes the techniques of suspension-, emulsion-, mini-, and microemulsion-polymerization as well as precipitation polymerization. Solvent is usually water, but heterophase polymerizations in inverse media are also examined. 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 in aindustrial 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 molecular level (synthesis of block & graft copolymers by emulsion polymerization) and on a colloidal level (core-shell latices, hollow spheres, colloidal superstructures) by a rational use of the particle interfaces and interface effects in heterophase polymerization (*Dr. Klaus Tauer*).

New Functional Polymers and Blockcopolymers
Amphiphilic polymers consist of components which dissolve in different media, e.g. a hydrophilic and a hydrophobic part. Since we are able to adjust both components sensitively to the dispersion medium as well as to the dispersant, amphiphilic polymers allow the stabilization of unusual dispersion problems. 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 wirh surfaces, we expect to discover "the fourth code" of polymeric secondary structure formation (*Dr. Bernhard Schmidt*)

· 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 is systematically explored (*Dr. Jiayin Yuan*)

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 include:

· Special techniques of transmission and scanning electron microscopy on soft, structured matter which are run at the base of a central service group (*Dr. Jürgen Hartmann*).

Materials for Energy Applications
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, methane activation, better batteries, ultra capacitors, remote energy storage, lightweight solar cells, all these topics are intimately connected with the control and design of materials nanostructure. Activities based in Golm include:

· New C/N-polymers and carbon materials to expand the property profile of carbon. Use of such materials as an electrode and electrocatalyst, both in batteries (metal/air, metal/sulfur) and in fuel cells. (*Dr. Tim Fellinger*).

· Metal free catalysis and photocatalysis with porous organic semiconductors: Novel synthesis schemes towards carbon nitrides (*Dr. Darya Dontsova*).

· Use of CN-materials for electrochemistry and photoelectrochemistry. Generation of new materials hybrid systems based on Ni and metalnitrides/metalcarbodiimides for hydrogen and oxygen generation (*Dr. Menny Shalom*)

· Superhigh surface area carbons and their use for supercapacitors, in-situ analysis of the charge storing process. Salt melt carbon synthesis and supramulecular approaches towards C_2N (*Dr. Nina Fechler*)

Colloid Chemistry for Green Chemistry, Green Polymers and Biorefining

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, *Dr. Davide Esposito* together with *Dr. Thomas Aicher/FHG*)

- Conversion of carbohydrates into lactic acid and other platform chemicals (*Dr. Davide Esposito*)

- Next Generation Green Polymers based on sustainable monomers (*Dr. Davide Esposito, Markus Antonietti, Dr. Bernhard Schmidt*)

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

De Novo Nanoparticles

Many materials, which are relevant for novel energy cycles and more efficient chemical reactions (catalysis) are not available as nanostructures (or their synthesis is not sustainable) so that "de novo" systems have to be designed from scratch.

- We develop new synthetic pathways towards special lead-based perowskite nanostructures for photovoltaics. (*Dr. Menny Shalom*)

- New cathode nanomaterials for the lithium battery are another target for novel nanostructures where progress will directly impact society (*Dr. Tim Fellinger*)

- Synthesis in interacting but not reactive salt melts is another way to unusual nanostructures (*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 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.

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 co-catalysts 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 (*Dr. Darya Dontsova, Dr. Menny Shalom, Dr. Tim Fellinger*).

Visions and Future Perspectives in the Director's Perspective 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. We completed the restructuration to enter a period with more coordinated research and longer term goals focused around the director and more tightly bound junior people. These people have already started (Dr. Fellinger, Dr. Esposito, Dr. Shalom, Dr. Fechler and Dr. Dontsova, in 2015: Dr. Schmidt) and are currently setting their corresponding profiles.

Our trials to cooperate with the National Excellence Centre on Catalysis of the TU Berlin are to my opinion in full bloom, 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 progressing with our activities to strengthen work projects between the departments, among them a "glycomaterials" project together with the Seeberger and the Fratzl department. Other potential projects which awaiting appropriate junior staff scientists are "gradient materials" and "soil colloids".

Markus Antonietti
Director of the Department
of Colloid Chemistry

PLANAR AMPHIPHILIC MONOLAYERS AT FLUID INTERFACES

Langmuir Monolayers as Model Systems in Biophysics, Colloid and Material Science

Gerald Brezesinski 02.04.1950
1974: Diploma, Biophysics (Lomonossow University of Moscow)
Thesis: The parametric pump – a physical-chemical model of the active transport of ions in cells
1981: PhD, Physical Chemistry (Martin Luther University of Halle/S.)
Thesis: Einfluss der chemischen Struktur auf das thermische Phasen- und Mischungsverhalten binärer und ternärer Phospholipid-Wasser-Systeme
1987: Habilitation, Colloid Chemistry (Martin Luther University of Halle/S.)
Thesis: Untersuchungen zum Phasen- und Mischungsverhalten ausgewählter Phospholipid-Wasser-Systeme
1981-1982: Postdoc (Biological Research Centre, Szeged, Hungary)
1982-1992: Research Scientist (Institute of Physical Chemistry, University of Halle/S.)
1992-1995: Research Scientist (Institute of Physical Chemistry, University of Mainz)
Since 1995: Group Leader (Max Planck Institute of Colloids and Interfaces, Potsdam)
Since 2009: apl. Professor, Physical Chemistry (University Potsdam)

References:

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[3] Stefaniu, C., Brezesinski, G.: X-ray investigation of monolayers formed at the soft air/water interface. Curr. Opin. Colloid In. **19,** 216-227 (2014).

Monomolecular films at the air/water interface are interesting model systems in biophysics, colloid and material science **[1]**. But the early work with amphiphile monolayers was largely hampered by the absence of tools to investigate liquid interfaces with molecular and microscopic resolution **[2, 3]**. Meanwhile, many highly surface sensitive techniques can be applied to study interactions of dissolved biomolecules (DNA **[4, 5]**, peptides **[6, 7]**, enzymes) or nanoparticles with model membranes to contribute to a better understanding of structure-function relationships. Additionally, the structures of thin layers of peptides confined to the soft air/liquid interface have been investigated and compared with structures obtained in bulk. Exciting and unprecedented results have been obtained by discovering a highly-ordered two-dimensional structure of glycolipid monolayers. Using a novel hexayne amphiphile as a reactive, carbon-rich sibling of typical fatty acid ester amphiphiles that formed well-ordered self-assembled monolayers at the air-water interface, self-supporting sp2-rich carbon nanosheets have been prepared at room temperature. In this report, the main results of our work concerning peptidomeimetics **[8, 9]**, glycosylphosphatidylinositols **[10, 11]**, and carbon nanosheets **[12]** will be described.

Selected Achievements

Precision Polymerfoldamers as Peptidomimetics

β^{3R6}-peptides (in cooperation with L. Hartmann, Department of Biomolecular Systems) have been studied in 2D and 3D in order to investigate their folding and aggregation behavior. Stable films of specifically designed oligomers can be formed on a buffer solution. All oligomers investigated contain a high amount of β-sheet-like structures, as seen by bands in the Amide I region between 1625 and 1645 cm^{1}.

Two representative oligomers were selected for GIXD experiments as they form strands which do and do not aggregate, respectively. The short oligomer **7** exhibits Bragg peaks in the wide- as well as in the small-angle regions (**Fig. 1**). The weak Bragg peak at 1.327 $Å^{-1}$ (**Fig. 1e**) corresponds to the interstrand distance of 4.735 Å defined by the hydrogen bonds in crystalline β-sheets (proved by IRRAS experiments showing a band at 1635 cm^{-1}). The other oligomer (**11**) does not show the characteristic Bragg peak in this region in good agreement with IRRAS data showing the amide I band only at a high wavenumber of 1641 cm^{-1}. This non-aggregated strand structure is characterized by the lack of long-range correlation between the strands. Additionally, both layers exhibit two-dimensional smectic order (Bragg peaks in the small-angle region). The higher longitudinal order of oligomer **11** can be attributed to electrostatic repulsion, since both ends are positively charged in contrast to oligomer **7.** The determined long repeat distances are shorter than expected for elongated strands.

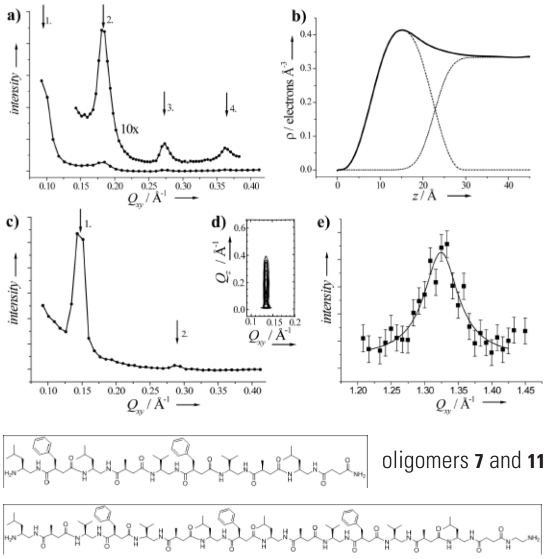

*Fig. 1: a) Corrected X-ray intensities versus the in-plane scattering vector component Q_{xy} for **11. b)** Electron density profile ρ(z) of **11** versus the vertical z coordinate. **c)** Corrected X-ray intensities versus the in-plane scattering vector component Q_{xy} for **7. d)** Contour plot of the corrected X-ray intensities as a function of in-plane (Q_{xy}) and out-of-plane (Q_z) scattering vector components of **7. e)** Corrected X-ray intensities versus the in-plane scattering vector component Q_{xy} for **7.** Note that the intensity of this Bragg peak is extremely small (large error bars). All experiments have been performed at the air/water interface at 20 °C and 20 mN/m.*

Subgel Phase Structure in Monolayers of Glycosylphosphatidylinositol Glycolipids

Glycosylphosphatidylinositols (GPIs), natural complex glycolipids essential for a range of biological functions, are poorly understood with regard to their interactions and arrangements in cellular membranes. To evaluate the role of the head group in the 2D structure formation three GPI-fragments (**Fig. 2A**) bearing the same hydrophobic part but different head groups have been investigated (in cooperation with D. Varón Silva and P.H. Seeberger, Department of Biomolecular Systems). Condensed monolayers of simple GPI fragments are defined only by ordered alkyl chains. The monolayers of more complex fragments are additionally characterized by highly ordered head groups (**Fig. 2B**). Due to the strong H-bond network formed by the head groups, GPI-fragment **3** both segregates and induces order in a model membrane phospholipid (POPC) that mimics the liquid-disordered phase of cell membranes. We have shown that the strong van der Waals interactions between hydrophobic chains overcome the head group interactions and dominate the structure formation in mixtures of GPI–fragment **3** with lipids **1** and **2** that form condensed phases. This behaviour can be linked to the GPIs affinity for lipid rafts.

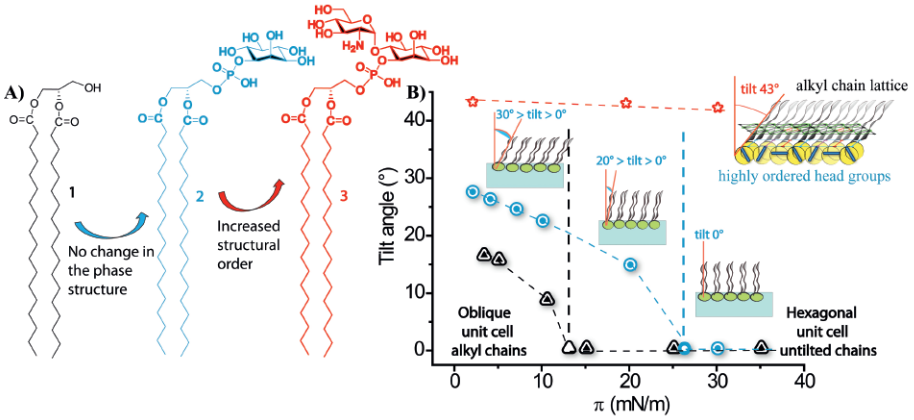

Fig. 2: A) Chemical structures of the three investigated GPI-fragments B) Comparative representation of the monolayer structural changes of the three GPI-fragments depicted by the variation of the tilt angle of the alkyl chains (t) with the lateral surface pressure (p) on PBS at 20 °C.

Functional Carbon Nanosheets

Carbon nanostructures including two-dimensionally extended nanosheets are promising components for technological applications, such as high performance composites, lithium storage, fuel cell technology, photovoltaics, or nanoelectronics. Chemical surface functionalization would render such structures better processable and more useful for tailored applications but is precluded by their thermolytic preparation. In cooperation with the group of H. Frauenrath (Ecole Polytechnique Fédérale de Lausanne, EPFL), a novel approach for the preparation of thin, two-dimensional carbon nanostructures with extended lateral dimensions based on the self-assembly and subsequent carbonization of a carbon-rich hexayne amphiphile at the air-water interface has been developed. The amphiphiles self-assembled into ordered monolayers which have been characterized by different experimental methods. The molecules form a distorted hexagonal 2D lattice (a = 5.20 Å, b = 6.25 Å, c = 6.29 Å with spacings determined by the size of the hydrated polar head group. The hexayne and dodecyl segments are closely packed and display tilt angles of 62.5° and 35.0° relative to the layer normal, respectively, resulting in an overall layer thickness of 2.6 nm. A detailed molecular model of the internal structure proved that the hexayne moieties were densely packed at π-π stacking distance, suitable for carbonization (carbon-carbon short contacts of 3.42–3.53 Å between acetylene carbons C1–C9 and C4'–C12' (along the a axis) and 3.60–3.78 Å between acetylene carbons C3–C8 and C7'–C12' (along the b axis) of neighboring molecules). The very tight packing of the hexayne segments within this less than 7 Å thick 'carbon precursor' sublayer was suitable for quantitative carbonization upon UV irradiation at room temperature (**Fig. 3**), producing sp^2-rich carbon nanosheets with a microstructure that resembled 'amorphous carbon' materials typically obtained after annealing at temperatures of 800–1000 °C. Mechanically stable and rigid carbon films with a molecularly defined thickness of 1.9 nm and lateral dimensions on the order of centimeters have been produced. These thin carbon nanosheets with their hydrophilic surface functionalization proved to be useful as low background contrast substrates for high resolution TEM imaging of specimen deposited from aqueous media.

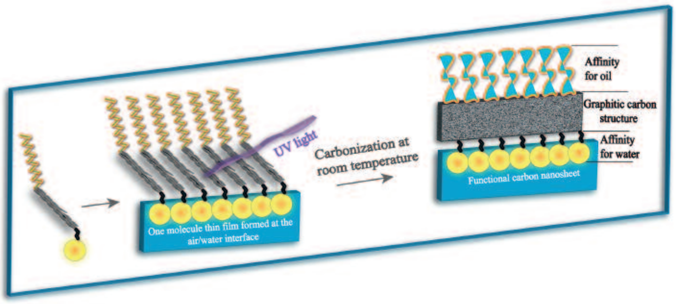

Fig. 3: The hexayne amphiphile was spread from a dilute chloroform solution onto the surface of Millipore water in a Langmuir trough.
Compression leads to a stable and tightly packed layer composed of essentially three segments: the hydrophobic dodecyl chain, the carbon-rich hexayne sublayer and the polar head group. Mild carbonization by UV irradiation at room temperature resulted in quantitative carbonization of the oligoynes within minutes. The self-supporting carbon nanosheets with macroscopic lateral dimensions exhibited a molecularly defined thickness of 1.9 nm and an 'amorphous carbon' microstructure.

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ARTIFICIAL PHOTOSYNTHESIS

Novel Approaches to Carbon Nitrides – Photocatalysts for Water Splitting

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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)

Since 11/2012: Research Group Leader Department of Colloid Chemistry (Max Planck Institute of Colloids and Interfaces)

Photocatalytic water splitting is an inexhaustible potential source of hydrogen which is the friendliest fuel to the environment. Hydrogen has the largest energy density and has recently emerged as a highly attractive alternative to depleting and expensive fossil fuels. However, photocatalytic water splitting requires large amount of input energy, and is still incompatible with existing energy generation technologies. Most of photocatalysts used for photocatalytic water reduction have disadvantages of absorbing only UV-light (e.g. TiO_2) which is only the minor fraction of solar light or suffer from photocorrosion. Graphitic carbon nitride based materials (having stoichiometry close to C_3N_4) represent a class of metal-free organic polymeric semiconductors that absorb the high energy part of visible light, and are typically prepared by thermal condensation of nitrogen-rich precursors, such as melamine, urea, cyanamide or dicyandiamide. However, products of bulk synthesis are characterized by low surface areas (1-10 m^2/g) and poor separation of photogenerated charge-carriers that leads to low reaction rates and quantum yields. Silica templates were previously used to prepare C_3N_4 with high (~200 m^2/g) surface areas, but these had to be removed using toxic HF sources.

Our group works on 1) development of alternative safe methods to obtain C_3N_4 with high surface areas, 2) improvement of charge-separation in C_3N_4 by tailoring its chemical structure or creating an efficient semiconductor heterojunction, and 3) elaboration of new synthesis strategies to C_3N_4.

Salt – Melt Assisted Synthesis

Running polymerization reactions in a suitable solvent may provide control over morphology, crystallinity and surface areas of the resulting polymers. Molten salts can potentially serve as high temperature solvents for condensation of C_3N_4 precursors if they have a suitable melting point, which is close to the onset of the first condensation step, and are dissolving C_3N_4 precursors and further reaction intermediates. Known examples are LiX/KX (X = Cl, Br) eutectics which are used to prepare crystalline poly(triazine imides)/LiX (PTI/LiX). We obtained different functional C_3N_4-related composites by performing the condensation in eutectics containing divalent metal chlorides as a main component. Selection of metal (M^{2+}) influences the strength of the corresponding Lewis acid, MCl_2 ($M = Zn^{2+}$, Sn^{2+}, Co^{2+}), and in this way defines the interaction between the salts and precursors.

Condensation of melamine in **$ZnCl_2$-containing eutectics** gives rise to novel PTI-based composites with the improved absorption in visible light range due to the formation of dyadic system between C_3N_4 and ZnO clusters or other Zn^{2+} containing species. Unlike LiX/KX (X=Cl, Br), $ZnCl_2$ being a *strong Lewis acid* plays a role of the reactive solvent during the synthesis, and binds strongly to the condensation intermediates. Adjustment of precursor concentration and a proper selection of the alkali metal chloride constituent of $MCl/ZnCl_2$ melt give a possibility to change the on-set of phase demixing, tune the interactions strength between the condensation intermediates and the solvent and vary the solubility of the intermediates in the melt. Overall, one can direct the reaction from zinc cyanamide to both crystalline poly(triazine imides) or amorphous MOF-like hybrid materials **(Fig. 1).** The latters have surface areas up to 700 m^2/g and turned out to be interesting as highly performing CO_2 adsorbents **[1]**

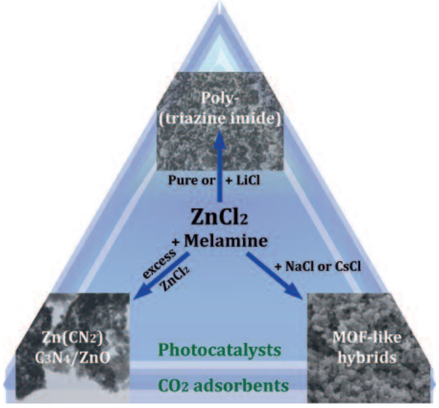

Fig. 1: Schematic illustration of possibilities provided by use of $ZnCl_2$-eutectics for C_3N_4 synthesis.

SnO_2/carbon nitride photocatalysts with surface areas up to 300 m^2/g were prepared by condensation of dicyandiamide in alkali metal chloride/**$SnCl_2$-containing salt melts** at 550 °C, without the use of hard templates. XPS, XRD and HR-TEM investigations showed that the obtained materials are composed of 5-10 nm SnO_2 nanoparticles deposited onto nanosheets set up from Sn-intercalated 1D-melon ribbons **(Fig. 2).** SnO_2/C_3N_4 composites are found to be highly efficient in the photocatalytic reactions, as exemplified by Rhodamine B degradation and water reduction (Pt is used as a co-catalyst). Under optimized synthesis conditions, these composites achieve hydrogen evolution rates more than two times higher than mesoporous graphitic carbon nitride (mpg-C_3N_4, s. a. ~200 m^2/g) under visible light irradiation. In principle, this new method based on utilization of $MCl/SnCl_2$ salt melts as a reaction medium allows carrying out various polymerization reactions in the presence of the *mild Lewis acid* in the solution phase in a wide temperature range of 180 – 550 °C. Moreover, $SnCl_2$ eutectics are even suitable for post-synthesis modification of bulk carbon nitride to retailor its morphology and greatly increase the surface area and photocatalytic activity **[2].**

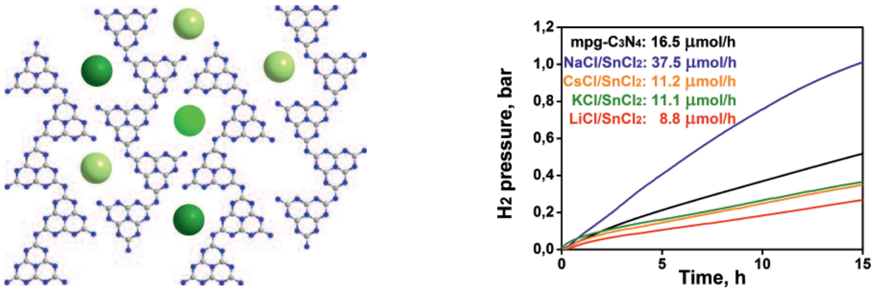

Fig. 2: Suggested structure of C_3N_4 prepared in $SnCl_2$-salt melts (left); photocatalytyic water reduction rates using SnO_2/C_3N_4 composites (right). Blue, grey and green spheres correspond to N, C and Sn atoms, respectively.

On its turn, eutectics containing **$CoCl_2$**, a *weak Lewis acid,* can serve as a reaction medium in single-step preparation of Co(II, III) oxide/C_3N_4 photocatalysts that show water oxidation efficiencies comparable to those of Co_3O_4 NP/C_3N_4 composites prepared in 3 steps **(Fig. 3)**. The chemical structure of C_3N_4 counterpart of composite can be conveniently adjusted by selection of second component of the salt melt, and alkali metal chlorides and $ZnCl_2$ give rise to PTI, while $SnCl_2$ results in melon polymers.

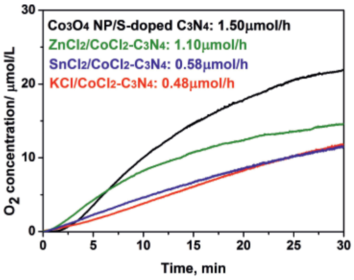

Fig. 3: Photocatalytic water oxidation by CoOx/C_3N_4 photocatalysts prepared in $CoCl_2$-containing salt melts.

Complex-Templating Method

Complex templating method combines the advantages of hard template method and phenomenon of supramolecular complex formation between molecules with complementary hydrogen bonding. Here, $Al(NO_3)_3{\cdot}9H_2O$ was successfully used as a “green template” and a hydrogen-bonding partner of melamine simultaneously providing a distinct porosity and defined particle morphology to the resulting carbon nitrides. Surface areas of final products (up to 90 m^2/g) are several times lower than those provided by SiO_2 templates, still, the benefits of $Al(NO_3)_3{\cdot}9H_2O$ are low cost and easy removal of its decomposition products after the synthesis. The developed synthesis procedure resulted in up to 20 times increase of the photocatalytic activity in comparison to the reference graphitic carbon nitride. The factors responsible for such a high activity are increased surface area and pore volume, as well as improved charge separation achieved by smaller grain size of photocatalysts and in-situ created heterojunction between melamine- and complex-derived carbon nitride phases.

1,2,4-Triazoles as New C_3N_4 Precursors

We found that the pyrolysis of electron-rich, but hydrogen poor precursors, 3,5-diamino-1,2,4-triazole and 3-amino-1,2,4-triazole-5-thiol, in bulk and in LiCl/KCl salt melt leads to the formation of carbon nitride materials with distinct linear, partially negatively charged, melon structure resembling the structure of emeraldine salts of polyaniline **(Fig. 4) [3].** The acidic character of the precursor expressed as an ability to undergo the replacement of imine-nitrogen with alkali metal is partially preserved by the final carbon nitride structures giving rise to the improved optical absorption and emission properties. This also comes with different electronic and crystalline structures when compared to all previously reported carbon nitride materials. All of the products are thermodynamically able to reduce water, and photocatalysts prepared from 3-amino-1,2,4-triazole-5-thiol in LiCl/KCl are 1.2 – 1.8 times more active than mpg-C_3N_4 in HER upon visible light irradiation. Such a high activity in spite of modest (30 m^2/g – 100 m^2/g) surface area of catalysts is attributed to the improved conductivity within the material and the resulting efficient charge separation of the photo-generated charge carriers.

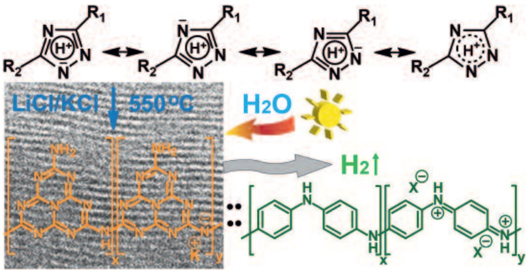

Fig. 4: Schematic illustration of preparation and photocatalytic properties of charged poly(heptazine imides) from substituted 1,2,4-triazoles.

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BIOMASS CONVERSION INTO BUILDING BLOCKS FOR COLLOIDS

Biorefinery and Sustainable Chemistry

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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 resources and 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 valorization 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 fine and platform chemicals 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 the upgrade of biomass into an array of valuable chemical for the generation of polymers and colloids. We are currently articulating our research around three major themes **(Fig. 1):** 1) the development of hydrothermal methods for biomass deconstruction, which enable the conversion of polysaccharides and lignin into an array of useful building blocks and platform chemicals; 2) the development of novel colloidal sustainable catalysts, to be evaluated during the catalytic upgrade of biomass derived substrates; 3) the synthesis of value-added products on the basis of sustainable building blocks that can be produced as the output of biorefinery conversion schemes.

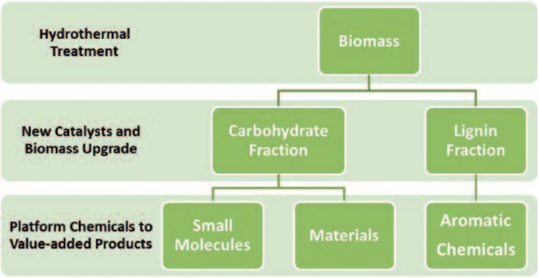

Fig. 1: Schematic Biorefinery

Hydrothermal 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 kind of treatments, we designed a new methodology that allow for the simultaneous isolation of an upgraded polysaccharide fraction **(Fig 2).** 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 could be isolated together with other organic acids, suggesting the possible use of this convenient method as entry point for new biorefinery schemes.

Fig. 2: A schematic representation of the hydrothermal deconstruction of biomass used to separate upgraded carbohydrate and lignin fractions ready for further processing or applications.

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, a green solvent with excellent properties as fuel additive **[2].** The functionalization of γ-valerolactone via α-methylenation has further being pursued, in order to obtain a monomer suitable for radical or emulsion polymerization. The preparation of latex particles on the basis of such monomer are currently investigated in collaboration with the group of Dr. Tauer (Colloid Chemistry), and will showcase an integrated refinery scheme capable of converting lignocellulosic feedstock into added-value nanomaterials.

Catalysts Development

Many of the primary products of the hydrothermal treatments of biomass can be conveniently upgraded into different platform chemicals by straightforward catalytic transformations. Unfortunately, many of these processes are catalyzed by expensive and rare elements belonging to the platinum-group metals. In addition, supported catalysts are often accessed via time-consuming synthetic procedures, besides being subjected to leaching and passivation when in contact with real biomass hydrolysates. The use of inexpensive and abundant elements, for example iron and nickel, for the synthesis of heterogeneous catalysts on the basis of simple protocols can positively influence the production of sustainable chemicals from biomass. In this context, carbon supported metals have been successfully applied as catalysts in the field of hydrogenolysis and hydrogenation. With this in mind, carbon supported Ni-Fe alloys were prepared by simple impregnation of cellulose from biomass followed by carbothermal reduction **[3].** This form of reductive treatment has proven ideal to generate carbon encapsulated nanoparticle as catalyst for the hydrogenolysis of biomass molecules, which are characterized by superior stability compared to the non-encapsulated commercial analogs. As an alternative approach, we are exploring the design and preparation of heterogeneous catalysts with precise tuning of the structure at the nanometer scale. We rely on the use of nitrides of non-rare metals. The hybridization of such materials with metal nanoparticles results in a completely new family of composites in which the activity of the metal is modulated by the electronic properties of the nitride support. For instance, we have recently showed how titanium nitride obtained as colloidal dispersion on amorphous or graphitic carbon can be efficiently used as support or promoter **[4].** In fact, the carbon matrix of this compound was successively doped with nickel nanoparticles to obtain composites with a high reactivity for the hydrogenolysis of aryl ethers and lignin fragments.

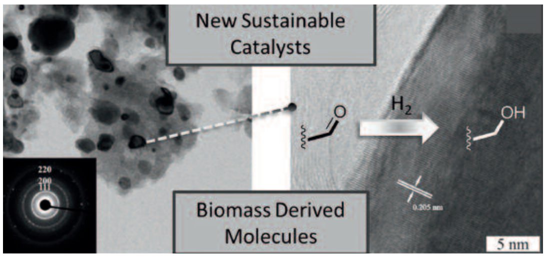

Fig. 3: Design of sustainable catalysts for the reductive upgrade of biomass molecules

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 find application in polymer and material sciences. One of our first goals in this direction was the development of green synthetic methods to access sustainable ionic liquids and imidazolium ions.

Fig. 3: New Value-added chemicals from biomass molecules

During the synthesis of lactic acid, pyruvaldehyde was identified as a valuable sustainable synthon **[1].** We further exploited it to synthesize a library of disubstituted imidazolium ions in combination with natural amino acids by using a green modification of the Debus-Radziszewski synthesis **[5].** The obtained compounds have proven as versatile building blocks for the preparations of task specific ionic liquids by simple acidification. Due to their functionalities, these compounds can found application in different areas, including the synthesis of poly(ionic-liquids) that we are exploring in collaboration with the group of Dr. Yuan (Colloid Chemistry). Additional studies on the reactivity of the bio-derived imidazolium ions are being conducted. As an example, we performed the hydrothermal decarboxylation of representative building blocks, which showed a great potential for the generation of a new family of ionic liquids exclusively derived from renewable precursors. Some of the so prepared ionic liquids are been exploited as reaction media for cross coupling reactions as well as cellulose and biomass dissolution **[6, 7, 8].**

Interestingly, imidazolium ions are common precursor of N-heterocyclic carbenes. On the basis of the substitution patterns derived from aminoacids, we are evaluating the possible use of the bio-derived imidazolium compounds as chelating N-heterocyclic carbenes for the generation of stable organometallic complexes. Alternatively, such compounds can be immobilized on solid supports and porous silicates to obtain heterogeneous-like ligands for different applications. Immobilization studies are being conducted in collaboration with the group of Prof. Hesemann (Université de Montpellier 2).

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RESEARCH COORDINATOR

Functional Carbon and Inorganic Materials via self-assembly

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Scientific questions have become very complex mostly requiring close co-working of disciplines, research institutions and industry. However, such structures demand for careful communication and organization. Here, my task is built on our opinion that it is time for rethinking common ways of practice and the believe that affiliation to both science and communications infrastructure is essential. 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 (international) partner institutions. This allows me to develop also my scientific profile which is also a prerequisite for an effective coordination of research.

A) Activities as a Research Coordinator

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, more specifically with water splitting as main focus. Within these activities, I'm responsible for the communication and matching of projects between the partners and within our department. In addition my group is actively participating in the projects which deal with the fabrication and investigation of carbons as catalyst support and as thermoelectric materials, respectively.

Along another path, we strive to link the binary program between the University of California Santa Barbara (UCSB), USA and the MPG also to the MPI of Colloids and Interfaces eventually establishing our institute as one of the main partners. Here my group is synergistically working together with the chemical engineering department at UCSB with the goal to investigate carbons and occurring respective (surface)processes during energy storage using solid state nuclear magnet resonance (NMR) spectroscopy. In this regard the design of suitable carbon materials is crucial and we developed a supramolecular approach towards highly nitrogen containing carbons with the possibility for ^{13}C- and ^{15}N-isotope labelling. This eventually makes the investigation of these commonly hardly detectable materials possible.

Within the so-called "111-project", I coordinate scientific operations between the Institute of Chemistry of the Chinese Academy of Science, China and the MPI of Colloids and Interface. Here, projects are very diversified, yet all have in common the integral aspect of surface phenomena. One of the first started projects concentrate on photo-switchable nitrogen-containing carbon materials (hydrophilic-hydrophobic) for controlled electrostriction.

Upcoming duties will include the coordination of novel European training networks (ITNs) as well as a potential bigger industrial cooperation within the concepts of biorefinery.

B) Activities as Research Team Leader

My group aims to make use of rational and simple synthesis schemes towards functional porous materials. So far, especially salts turned out to be highly versatile alternatives for the generation of nanoporous structures. In this report, the examples of carbons, carbon composites and oxides will be shown.

A second way I intend to follow is the supramolecular approach where we currently make use of preorganization schemes mediated through strong but non-covalent and thus reversible interactions. Recent activities include the use of well-chosen precursors to generate pre-defined, more ordered and nanostructured carbons, metal coordination to design crystalline phenolic materials and new approaches towards the utilization of natural building blocks for the generation of porous materials with high degree of chemical surface functionality.

As my group just started recently, this report is more a description of future concepts while I can only present the most important results for the salt templating approach.

Nanoporous Carbons

Functional carbons and composites became recently some of the most useful and versatile materials as they possess a variety of important and adjustable properties while costs are rather low. The final materials properties can be influenced, besides others, on the molecular as well as morphological level and incorporation of heteroatoms such as nitrogen into the carbon lattice, metals or porosity turned out to be highly powerful. Here, not only the chemical but also physical properties can be altered e.g. electronic conductivity and (oxidation) stability eventually leading to increased (electro)catalytic activity. Until today the fundamental principles for these phenomena are still not clear, yet the interplay of electronic states, heteroatom incorporation and morphology are suspected to play key roles.**[6]**

Eventually, the development of more efficient and sustainable synthesis approaches for nanoporous materials is highly demanding.**[5]** However, besides the quest for convenient precursors, hard templating or activation processes still have to be applied. Major drawbacks are the use of hazardous chemicals for the template removal and multiple, rather energy consuming synthesis steps. In order to circumvent this, we invented a new tool called „salt templating" allowing for the synthesis of a variety of porous material classes, e.g. functional carbons, carbon-based composites and oxides. **[7, 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. This unique synthesis gives access to a wide variety of compositions, morphologies and porosities where the appropriate choice of salts controls the pore size, architecture on the nanoscale and particle size. The pore size can correspond to ion pairs, ion pair clusters and their geometric percolation structures **(Fig. 1).**

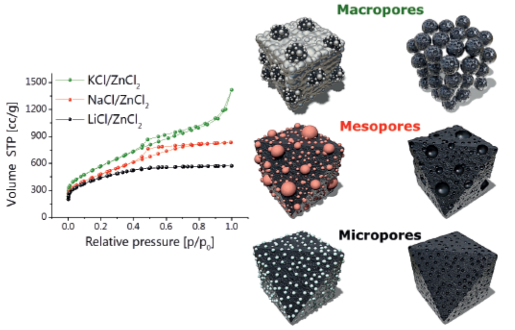

Fig. 1: Left: nitrogen sorption isotherms of carbons prepared with the same precursor but different template salts, (surface areas 2000 m^{2}g^{-1}; right: illustration of the different demixing processes during the synthesis leading to micropores (bottom), mesopores (middle) and porous spheres & macropores (top).

Contrary to current methods, it is possible to proceed in a single-step synthesis, while the porogen can easily be removed with water and in principal recovered afterwards for further use. Additionally, we were able to show that the final materials are, besides others, very suitable for energy storage and conversion.**[1, 2]**

Nanoporous Composites

Exemplarily shown for (but not restricted to) ionic liquids (IL) as precursors, the IL constitutes the nitrogen-doped carbon matrix and also acts as nitrogen source, here for metal nitride formation. After aqueous removal of the salt phase, e.g. vanadium nitride nanoparticles embedded in a nitrogen-doped carbon matrix with surface areas of up to 2400 m^{2}g^{-1}, are obtained **(Fig. 2).**

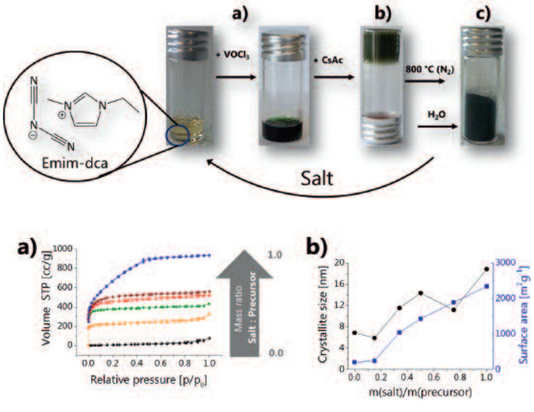

Fig. 2: top: a) addition of a vanadium precursor to the IL Emim-dca leads to a green complex, b) further addition of the template salt caesium acetate generates a glassy precursor, c) after heat treatment under inert atmosphere and aqueous removal of template salt highly porous vanadium nitride carbon composites are obtained. Bottom: a) increasing salt amounts result in increasing surface areas and pore sizes, b) surface area and vanadium nitride particle size in dependence on the salt amount.

Adding to the simplicity of the salt templating approach, it serves as a platform toward the rational design of nanoporous materials in a more sustainable fashion.

Nanoporous Oxide Powders and Aerogels

By exchanging the precursor, the broader application of salts for the synthesis of highly porous materials could be demonstrated, too. Here, the synthesis of porous oxides such as silicates and titania were tested for proof of principle even allowing for the synthesis of aerogels under ambient conditions **(Fig. 3).[4, 8]**

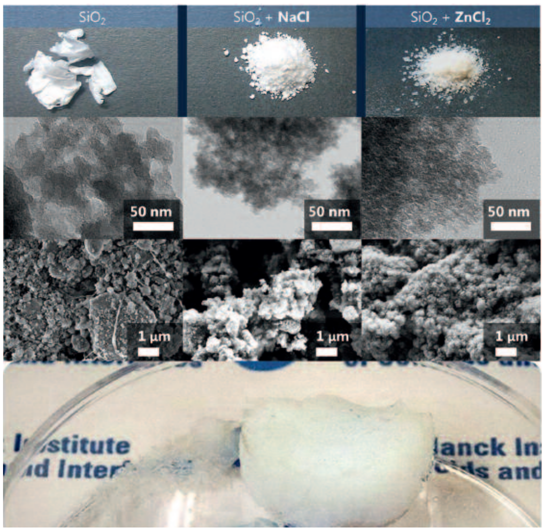

Fig. 3: Silicates synthesized without salt (left), with NaCl (middle) and ZnCl$_2$ (right). First row: macroscopic appearance, middle row: SEM, bottom row: TEM picures. Bottom: photo of a silica aerogel synthesized in the presence of ZnCl$_2$ under ambient conditions.

It could be shown that similarly to the carbons and composites the salt nature and amount strongly influences the materials structures on the nanometer scale resulting in highly porous oxides.

Fine tuning of the process additionally allows for the synthesis of silica aerogels under abmient conditions, thus conventional supercritica CO$_2$ drying is not need anymore **(Fig. 3).**

In general, the examples already shows the beauty and at the same time power of simple processes. My group aims to extend the demonstrated possibilities also with respect to processing such as porous film formation as well as preorganization. Especially with regard to carbons, we want to make use of the significant materials property changes due to differences on the molecular scale. For example, carbons can be conductors or semiconductors, and we believe that the right combination of different carbon families will allow for the fabrication of all-carbon composites. Furthermore, through rational choice and preorganization of functional groups we aim to generate materials with custom-made properties for energy storage and conversion.

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CARBON MATERIALS AND ELECTROCHEMICAL ENERGY APPLICATIONS

Teaching Catalysis to Carbon

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Introduction

Carbon nanomaterials, due to their unique properties, are one of the most important materials in applications including adsorption, separation, energy conversion and storage **[1].** The key-drawback in the synthesis is still the necessity of using templates and structure directing agents, which have to be pre-synthesized and/or removed in a separate step, to obtain porosity, high surface area or special shapes and morphologies. Moreover such carbonizations are typically carried out in solid-state transformations, which are inherently limited in there reorganizational dynamics. From an application point of view carbon materials, e.g. heteroatom-doped carbons are very promising, especially in the topical area of electrocatalysis, such as in the oxygen reduction/evolution reaction (ORR/OER). Recent reports suggest that increased Fermi levels may lead to improved electrocatalytic activity and stability **[2]**. As heterojunctions are a feasible way for modification of the electronic band structure, hybrid carbon-inorganic materials are a key target in this research.

Carbon and Carbon-Inorganic Hybrid Aerogels as Efficient Electrocatalysts

Previously, we reported on a novel one-step salt templating carbonization route using inorganic salt melts to prepare highly microporous nitrogen doped carbons with surface areas >2000m^2g^{-1} **[3]** The salt melts (e.g. eutectic $KCl/ZnCl_2$) act as solvents and porogens with a broad temperature window, in which microporous carbons and depending on the salt to precursor ratio also meso- and macroporous carbons can be obtained. Carbonizable ionic liquids are used as precursors as they form homogeneous melts with the inorganic salts as an essential requirement for a well-controlled process. In some recent work we optimized the synthesis conditions including the salt to precursor ratio and obtained highly porous and high surface area nitrogen doped carbon aerogels, which naturally possess a mass transport porosity, which is desired in electrocatalysis. The reaction scheme is shown in **Fig. 1.**

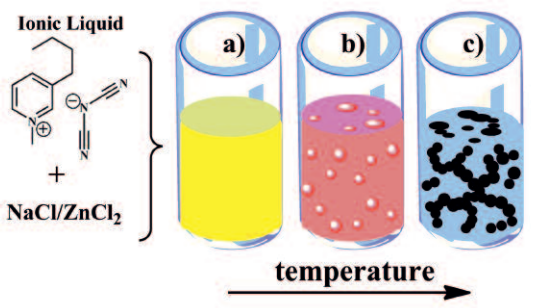

Fig. 1: Ionothermal Carbonization of Ionic Liquid in Inorganic Salt Melt

The carbon aerogels, synthesized with this easy-to-do procedure show very high mass activities in the important ORR and have equal performance like expensive platinum based commercial catalysts in the alkaline medium **(Fig. 2) [4].**

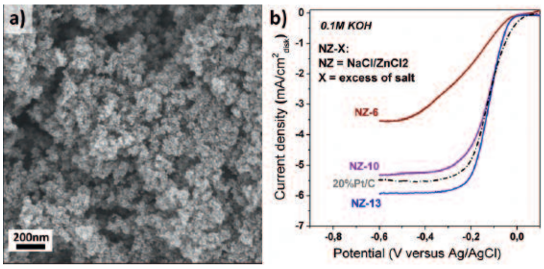

Fig. 2: a) SEM image of the N doped aerogel; b) ORR polarization curves in alkaline medium at 1600 rpm

In a similar approach we expanded this innovative synthetic approach towards non-noble metal containing hybrid materials, by using another ionic liquid precursor and in addition simple iron salts. The specific ionic liquids based carbon hardly undergoes carbothermal reduction even at temperatures as high as 850°C. Therefore, the iron ions remain homogeneously coordinated to the nitrogen doped carbon scaffold and together efficiently catalyze ORR with improved performances also in acidic medium **[5].**

Hybrid Materials Based on Heteroatom Doped Carbons as Bifunctional Mott-Schottky Catalysts

The heterojunction between two materials with different electronic properties leads to an exchange of electron density, which is accompanied with the bending of electronic bands. The resulting modified electronic properties of the junction can enhance catalytic properties, which is referred to as Mott-Schottky catalysis **[6].** Recent reports suggest that the ORR process at nitrogen doped carbons is an outer sphere mechanism and that the position of the Fermi level is the key-descriptor for the activity. High potentials for OER, but also ORR give rise to carbon oxidation as a main issue with regard to the catalytic stability. A reduced energy of the valence band of heteroatom doped carbon should improve the critical oxidation stability. We recently reported on two novel carbon hybrid systems, where synergistic effects on the catalytic properties could be observed. In one example, we employed common filter paper, which is composed of cellulose as a sustainable carbon precursor and structural template at the same time. After infiltration with phenanthroline, and nickel acetate, followed by thermal treatment to 800°C, we obtained a porous nitrogen doped carbon scaffold with strongly attached and nitrogen-coordinated nickel/nickel oxide nanoparticles with the size of ~ 14nm. Interestingly the hybrid material shows increased catalytic activity towards OER as compared to the equivalent material without nitrogen binding sites. Coordination and strong attachment create heterojunctions, which favorably influence the electronic properties of the hybrid material leading to the enhanced catalytic performance.

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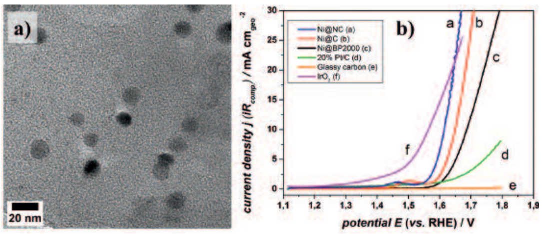

Fig. 3: a) TEM image of Ni@NC sample; b) OER performance of Ni@NC compared to a number of reference catalysts

In addition, the material is also an efficient hydrogen evolution catalyst and could be used for the construction of a symmetric electrolyzer with the theoretical efficiency of 68% at 10mAcm^2 **[7].** In another example we generated cheap and sustainable porous carbon by employment of nanosized $CaCO_3$ as sacrificial template using dry pig blood powder as the carbon source. Inside the porous and heteroatom doped (N, S and P sites) we grew Co_3O_4 nanoparticles, which were well-dispersed and again strongly bound to the carbon backbone. Also in this case we found strong enhancement of the catalytic activity. Herein, the hybrid material performed better in ORR than the pure heteroatom doped carbon, but at the same time the performance in OER was also enhanced compared to Co_3O_4 bound to an undoped carbon **(Fig. 4).**

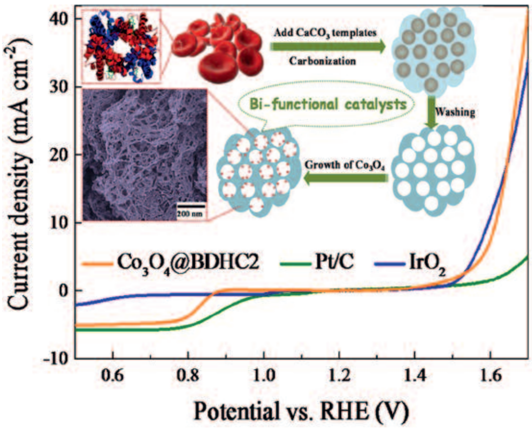

Fig. 4: Illustration of the preparation process and the electrocatalytic performance towards ORR and OER compared to reference catalysts

That means the heterojunction herein leads to synergistic enhancement of the catalytic activity of both compounds at the same time. This bifunctional catalyst could be used either in a fuel cell or in an electrolyzer mode **[8].**

Novel Ionothermal Carbon Superstructures

Continuing the research of the innovative and uncommon use of inorganic salt melts as reaction medium for carbonizations we recently had a break-through in terms of novel structure formations. We could observe the formation of vertically aligned graphene sheets performing carbonization of ionic liquids in molten zinc chloride and on the surface of nickel foam. For mechanistic considerations a blind experiment was performed. The ionic liquid precursor was wetted on the nickel foam and carbonized in absence of inorganic salt melt. Instead of nanosheets we obtained bamboo-like carbon nanotubes. The synthesis scheme, as well as the results of the blind experiment and the interesting superstructure are illustrated in **Fig. 5.**

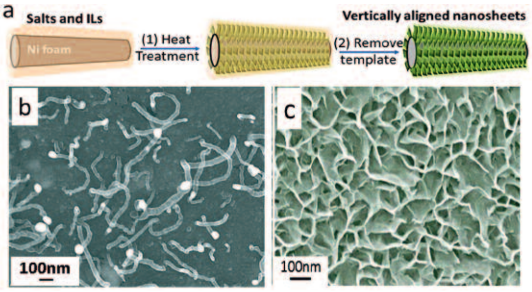

Fig. 5: a) Scheme of the synthesis process; b) SEM image of the blind experiment; c) SEM image of vertically aligned carbon nanosheets on a nickel foam

These results emphasize the importance of the nickel surface for heterogeneous nucleation and graphitization via the dissolution/precipitation mechanism, whereas the preferential growth of CNSs is aided by the presence of inorganic salt melt **[9].** Further on, we introduced the first thermal carbonization approach directly in solution. We used molten $ZnCl_2$ at 550° C and directly pyrolyzed hot-injected common organic solvents like ethanol, acetone, DMSO, acetonitrile, ethylene glycol or pyridine. The combination of ionothermal synthesis and the hot-injection technique leads to novel solvent derived nanocarbons with three distinct morphologies: spherical, sheet-like and branched nanofibers.

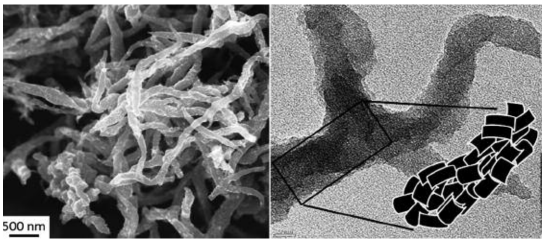

Fig. 6: Carbon after instant ionothermal carbonization of organic solvents

Contrary to possible extensive evaporation the solvents are carbonized quite efficiently, with sometimes surprising high yields. When heteroatom containing solvents were used, the doping levels reached up to 14 wt.% nitrogen and 13 wt.% sulfur. Like observed for other ionothermal carbonizations, in some cases high surface area solvent carbons (up to 1666 m^2g^{-1}) were obtained. Importantly, the nanofibrous morphology was explained by vectorial alignment of nanographenes, which herein act as carbon nuclei **(Fig. 6) [10].** Such oriented attachment mechanism was so far not reported for carbon, but is a well-known process in inorganic chemistry **[11].**

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MODERN TECHNIQUES OF COLLOID ANALYSIS

Electron Microscopic Studies of Colloidal Systems and Interfaces

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Transmission electron microscopy an scanning electron microscopy are suitable techniques to investigate the morphological structure of synthetic polymeric and inorganic particles, emulsions, polymeric membranes, mesoporous carbon, interfaces and composite materials and naturally-grown biomaterials on the micro- and nanometer scale. The determination of structural parameters such as the size and size distribution of colloidal particle systems, the pore size of mesostructured networks, the shape and the spatial arrangement of nanoparticles and their crystallinity are in focus on our electron microscopic research. Using cryo-scanning electron microscopy the internal morphological structure of aqueous systems like concentrated water/oil emulsions can be characterized. Because of the organization of the institute, there are many closed co-operations between the electron microscopy group and other research groups. Some of the interesting results of electron microscopic investigations are presented in the following.

The synthesis of non-spherical particles made of hydrophobic polymers requires special actions and frequently multi-step procedures. However, to conclude from the observed shape in the dry state on electron micrographs to the real state in the aqueous dispersion is not always possible because amphiphilic particles can change shape, morphology, and size in the dispersed state in dependence on concentration and ionic strength. Due to their chemical structure, cyclodextrins appear promising reductants for the redox-initiation of aqueous heterophase polymerizations with ceric ions. Using β-cyclodextrin (β-CD) as reductant in the ceric ion redox initiation of aqueous heterophase polymerization of N-isopropylacrylamide leads to latex particles with unprecedented morphology **[1]**. In **Fig. 1a, b** the synthesized particles appear as a stable assembly of polystyrene particles linked together with poly (N-isopropylacrylamide) (PNIPAM). The size of the β-CD–PNIPAM - polystyrene clusters is in a range of 2-4 µm and the diameter of the spherical polystyrene particles inside the cluster is between 20 and 200 nm. Comparing the morphology of the cluster in the dried state similar to their structure in the presence of the aqueous phase in the cryo-fixed state, in both the polystyrene particles are bounded inside the β-CD – PNIPAM complex **(Fig. 1c)**. The cryo-SEM micrograph **(Fig. 1d)** shows the anticipated 3D morphology of a cluster containing smaller polystyrene particles after freeze drying. A cluster that piles up on the fracture plane can be considered as lucky occurrence revealing, however, the 3D structure in the dispersed state. This new strategy for the synthesis of colloidal particles assemblies has a great potential for developments of new and so far unattainable colloidal morphologies.

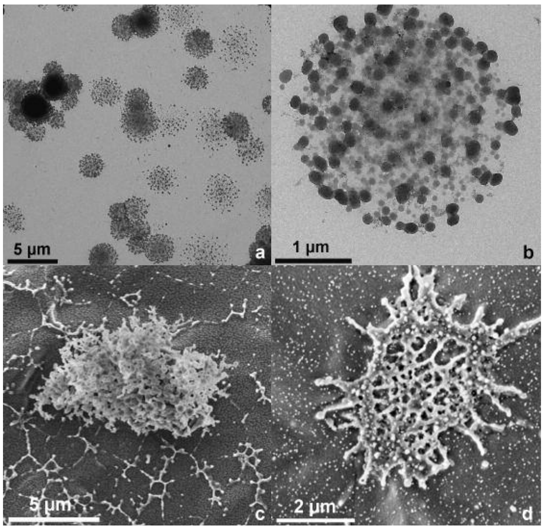

Fig. 1: Spherical assembly of primarily β-CD–PNIPAM - polystyrene clusters (a), the typical morphology of a single cluster (b) and a freeze-fractured (c) and a freeze-dried (d) β-CD –PNIPAM - polystyrene cluster of concentrated aqueous dispersion (solids content of 5 wt%).

Despite numerous methods that have been successfully applied for the fabrication of micro scaled carriers filled by hydrophobic substances, continuous efforts are made to develop new encapsulation techniques.

The ultrasonication technique is most promising for the simultaneous encapsulation of prepared emulsion droplets of a mixture of polymer solution and water-immiscible liquid. Microcapsule shells composed of polymer are synthesized at the interface between oil and the polymer solution.

Here, a new class of oil-filled microcontainers with core-shell morphology is presented, which can be prepared in one-step procedure by applying a low-frequency ultrasonic treatment **[3]**.

A mixture of chitosan and xanthan gum was layered with nonaqueous liquids and exposed to high-intensity ultrasonication. Cross-linking of both polysaccharides due to chemical interactions between their amino, hydroxyl, and carboxyl functional groups is induced by high energy ultrasound treatment. It leads to the formation of a stable layer at the droplet surface and, subsequently, to the formation of permanent shells of microcontainers, loaded with different types of "oils", such as miglyol, soybean oil, hexane, cyclohexane, and toluene. By varying the soybean oil/water ratio (from 1:300 to 1:1.5, respectively) the size the containers is varying in a wide range (300 nm to 8000 nm) **(Fig. 2)**. The thin external polymer shell covers the inner container core. The estimated thickness of the shell is 7-10 nm, which, however, is robust enough to keep the microcontainers stable during storage at 4°C for at least 6 months.

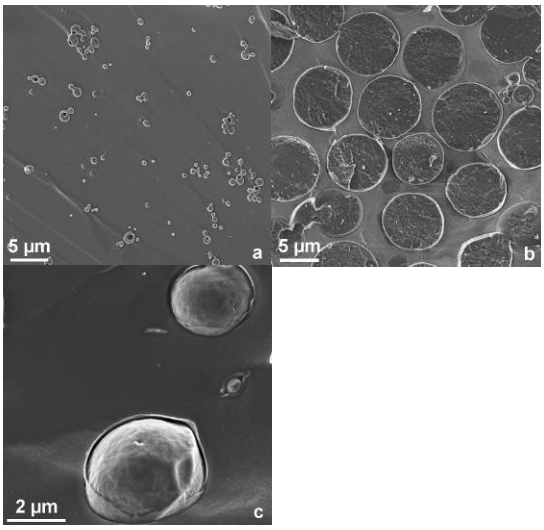

Fig. 2: Microcontainers with different size: (a) 1160 nm (PDI = 0.417), soybean oil/water ratio 1/60; (b) 7325 nm (PDI = 0.146), soybean oil/water ratio 1/1.5; and (c) containers with broken shells.

The used shell components-polysaccharides, chitosan, and xanthan gum are biocompatible, biodegradable, and lack allergenicity. These containers can be further modified upon demand with oppositely charged polyelectrolytes and/or particles.

High biocompatibility and biodegradability of proteins as material for the containers' buildup can be considered as benefits for their potential application.

The electrochemical conversion of the O^{2}-/oxygen couple is important for the next-generation energy technologies including metal-air batteries and devices, which can be reversibly used as water electrolyzer and fuel cell **[4].** Herein, we present a method that enables facile and scalable preparation of foam-like porous heteroatom doped carbon / Co_3O_4 nanoparticle hybrid materials using conventional blood powder (BP) as a unique carbon precursor and commercial $CaCO_3$ nanoparticles as template, with a particle size in the range of 10-100 nm with a narrow distribution.

During the solid state grinding the precursor and $CaCO_3$ template are successfully homogenized before the carbonization process. After carbonization Co_3O_4 nanoparticles were deposited onto the blood powder derived heteroatom doped carbon (BDHC) by a one-pot thermal deposition technique.

The utilization of nanosized $CaCO_3$ with a particle size of around 25 nm as a hard template/activating agent, it is interesting to find that highly porous BDHCs with variable morphologies can be obtained by changing the initial mass ratios of BP to $CaCO_3$.

For the initial ratio of BP:$CaCO_3$ = 2:1 (BDHC-2:1), the prepared carbon offers an interconnected mesoporous structure. The spherical pore shape and pore size is similar to the particle size of the used $CaCO_3$ nanospheres. This indicates, that the $CaCO_3$ particles were embedded into the precursor matrix to act as hard templates for the generation of mesopores **(Fig. 3a, b).** When the relative amount of $CaCO_3$ was increased (BP:$CaCO_3$ = 1:1) a highly porous carbon (BDHC-1:1) with a foam-like morphology, composed of a fibrous network was found.

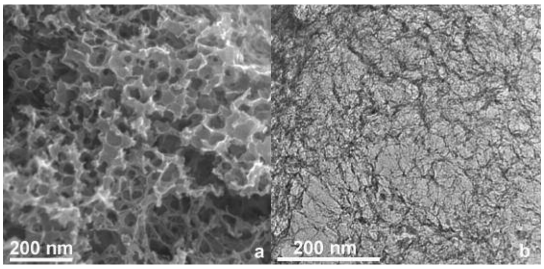

Fig. 3: Mesoporous morphology of BDHC-2:1; REM (a) and TEM (b)

Co_3O_4 nanoparticles with a size smaller than 10 nm and in the range of 20 nm to 40 nm were found for Co_3O_4@BDHC2. **Fig. 4 a, b** shows bright-field and dark-field TEM micrographs recorded on the same area of the Co_3O_4@BDHC2 sample. As can be seen in the dark-field image, the Co_3O_4 nanoparticles with bright contrast are uniformly embedded in the continuous foam-like carbon matrix.

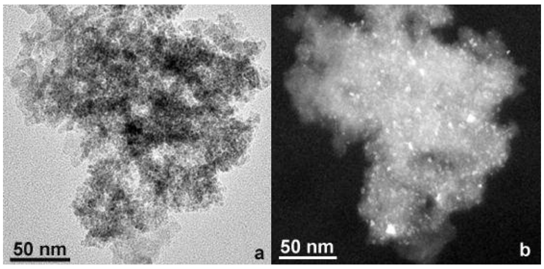

Fig.4: TEM micrographs of Co_3O_4 nanoparticles in the BDHC2-system a) Bright-field and b) Dark-field imaging

The mesoporous fibrous network structure of the blood powder derived heteroatom doped carbon results from the concerted action of hard templating and activation using $CaCO_3$ nanoparticles. The high surface area and strongly heteroatom doped material features stable anchoring sites for the immobilization of Co_3O_4, which greatly reduce the aggregation and growth of the decorated Co_3O_4 nanoparticles and improve the charge transfer between the two species **[4].**

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Materials for Renewable Energy Production

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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).

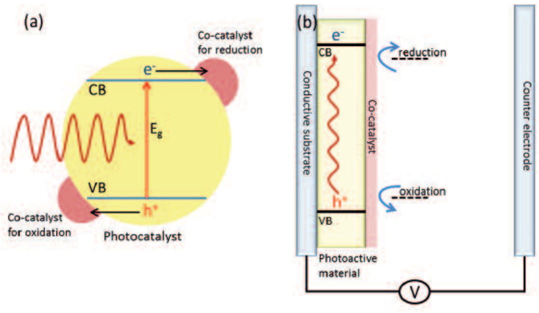

Fig. 1: Illustration of two photocatalysis systems

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 (C_3N_4) 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.

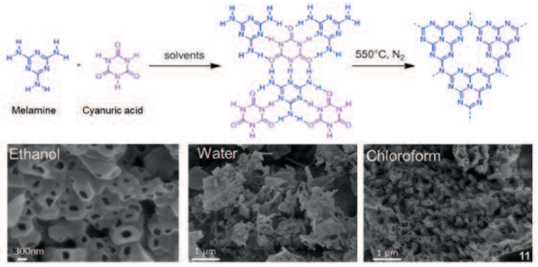

Fig. 2: A graphic presentation of hydrogen-bonded supramolecular complex and the resulting carbon nitride materials in different solvents

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.

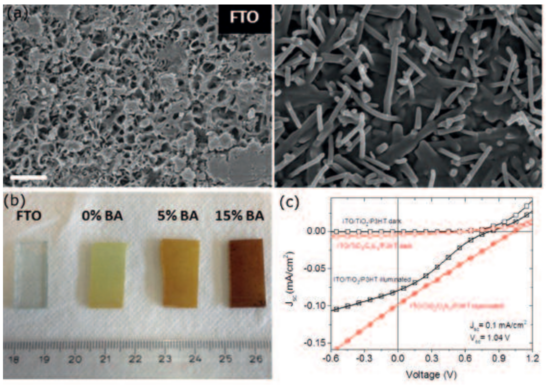

Fig. 3: (a) SEM images of carbon nitride deposited on FTO and glass. (b) Photograph of bare FTO and FTO with C_3N_4 films modified by different amounts of carbon. (c) J-V curves of $TiO_2/C_3N_4/P3HT$ and $TiO_2/P3HT$ solar cells measured in darkness and under 100 mW/cm^2 AM 1.5G illumination.

Non Noble Metals Based Materials for Energy Related Applications

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 and Ni_3N), partly embedded in an amorphous matrix of a carbon-nitrogen material **[7]**. Moreover, we demonstrated the ability to dope these materials with other metals (Mn, Co and Fe). The obtained materials show remarkable performance in the electrochemical production of hydrogen both in terms of low overpotential and high current densities. In addition, we found that the electrochemical properties of Ni-based materials can be altered by simple annealing, resulting in the formation of metal oxides on the surface alongside an increase in surface area **[8]**. Consequently, after oxidation, the electrocatalysts demonstrate high activity in OER. In sum, the activity of the highly porous material can be easily tuned from HER to OER only by simple thermal treatment in air, leading to a 70% overall water splitting efficiency.

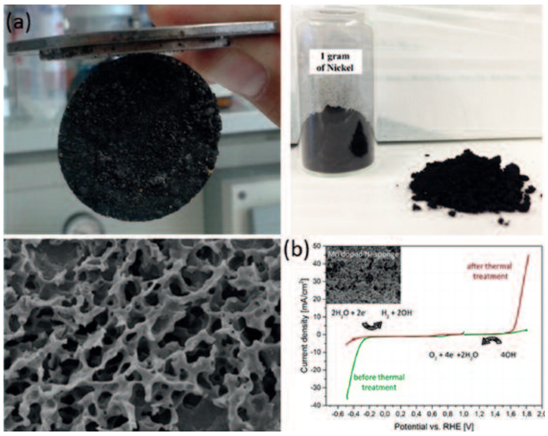

Fig. 4: (a) ~3g of sponge-like Ni that was prepared in one crucible (before and after grinding and washing with water) and the corresponding SEM image. (b) Linear sweep voltammetry of Ni-based material before and after surface activation which shows the HER and OER activity.

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Polymer Dispersions/Heterophase Polymerizations

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Despite the fact that the various heterophase polymerizations (HP) are centennial technologies, the formulation of general mechanistic aspects is still an unsolved issue. Better understanding of HP and educating students on this topic is of general scientific and economic interest and a goal that it is in the very core of the activities of our research. Amongst others the following results have been published 2013-14.

Colloidal Aspects of Heterophase Polymerization – Pressures, Polymers, Particles

The action of pressure during the different heterophase polymerizations is the common ground which allows a unified consideration. Besides the overall pressure which in a certain range can be controlled by the experimenter, the pressures dictated by the colloidal nature of the reaction system – the Laplace (P_L) and the swelling pressure (P_S) – are important. The importance of P_L and P_S on the events in the course of the reaction changes primarily in dependence on the composition of the droplets. **Fig. 1** summarizes our findings **[1].**

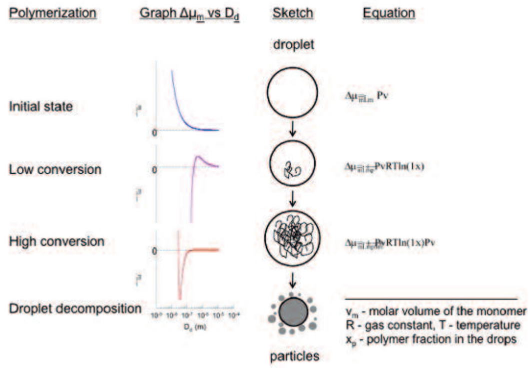


Fig. 1: Sketch how pressures influence HP initiated in monomer droplets; the middle part sketches the transition from a single monomer droplet (initial situation) to many polymer particles in the final dispersion; the equations on the right hand side show the contributions to the chemical potential of the droplets in the various states of the polymerization and the corresponding graphs on the left hand side illustrate the excess chemical potential ($\Delta\mu$m) in dependence on the droplet size ($\Delta\delta$)

Heterophase Polymerization in the Presence of Monomer Droplets

There are two fundamentally different strategies to carry out heterophase polymerizations, either in the presence or absence of monomer droplets. Here we restrict the discussion to the situation where monomer drops are present prior to polymerization. Under such condition HP is a transition between different colloidal states (from emulsion to suspension) controlled by polymerization. The key issue in this context is the role of monomer droplets. Their size is an important parameter essentially governing the process **[2].** Initiation inside the monomer drops happens with all initiators. It happens more frequently the higher the solubility of the initiator in the monomer phase. Polymer formation causes a stabilization of the droplet against Ostwald ripening because the insolubility of the polymer in the aqueous phase counteracts the Laplace pressure *(situation at low conversion of* **Fig. 1).** Further increasing x_p leads to rising swelling pressure which causes a volume increase of the particles. The swelling pressure can be so strong that tiny droplets are expelled *(situation at high conversion of* **Fig. 1).** The fate of the expelled droplets depends strongly on the stabilizing conditions (properties and concentration of the stabilizer). Quite importantly with respect to generalization, these ideas are independent of the particular polymerization conditions as demonstrated experimentally **[1].** However, the proportion of both the small and the large particles is controlled by the polymerization conditions, particularly by the nature of the initiator (hydrophobic or hydrophilic **(Fig. 2, 3)** for poly(vinyl alcohol) stabilizer). In each case a very specific morphology of the particles is observed, resembling colloidosomes – large cores covered by much smaller particles.

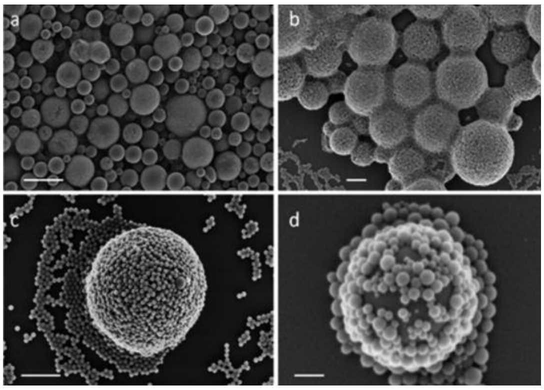


Fig. 2: SEM micrographs of PS particles made with hydrophobic initiators V65 (a, c) and BPO (b, d); the bar indicates 20 µm (a), 2 µm (b and c), 300 nm (d)

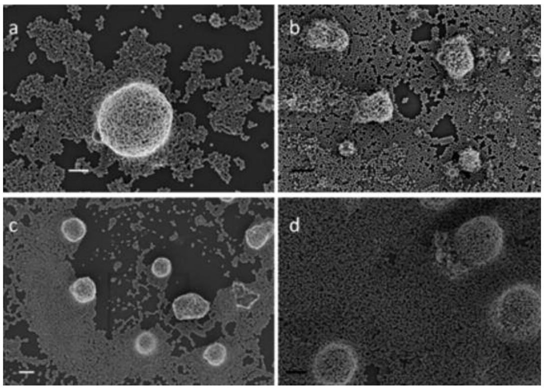


Fig. 3: SEM micrographs of PS particles made with hydrophilic initiators KPS (a), VA-086 (b), V501 (c), and V50 (d); the bar indicates 2 µm (a, b, d) and 3 µm (c)

How Much Weighs the Swelling Pressure

We developed a new method to follow (almost) isochoric swelling of gels by measuring the apparent weight increase after establishing the contact between the confined gel sample and the swelling agent **[3].** The gel is located inside a confinement cell with porous walls which is completely immersed in an arbitrarily large pool of the swelling agent. The whole setup is placed on a scale with the confinement cell being tightly connected to an external reference point in a way that the force is redirected almost completely towards the scale. This arrangement permits easily to modify the conditions inside the reservoir of the swelling agent during the swelling process **(Fig. 4).** Moreover, this technically simple method allows quite convincingly illustrating the action of the chemical potential.

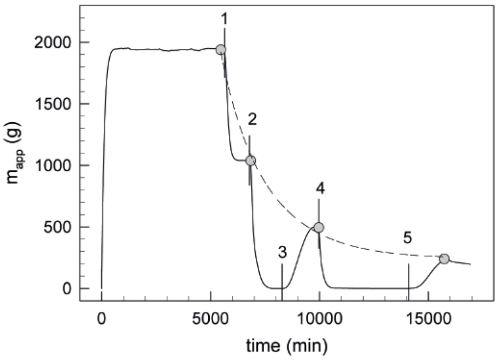
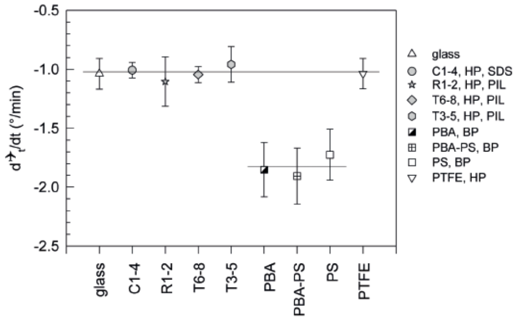


Fig. 4: Change of the apparent mass (m_{app}) of a PAA gel in pure water (from time 0 to point 1) and after alternating addition of sodium hydroxide solution and sulphuric acid; the amounts of base and acid added were adjusted to achieve after each addition a pH of about 13 and 1; the dashed line is a fit of the grey points and describes the response of the swollen gel under basic conditions on the ionic strength which increases from point 1 (pure water) to point 5 up to a value of about 5.5 M

The Wettability of Polymer Films Depends on the Polymerization Conditions

The polymerization conditions have a strong influence on the barrier properties of polymeric films. For a given copolymer composition, the recipe components of emulsion copolymer films clearly influence the initial static water contact angle, a measure of hydrophilicity. Common emulsifiers such as sodium dodecyl sulphate (SDS) cause lower contact angles than poly(ionic liquid) (PIL) dispersions which are a new class of stabilizers for heterophase polymerization **[4, 5].** In contrast, the time-dependent properties of the water contact angle reflect the given hydrophilic/hydrophobic conditions during the polymerization. Water-born emulsion copolymers (the upper data points of **Fig. 5**) show a distinctly different time-dependence of the contact angle than bulk polymers (lower data points of **Fig. 5**) of the same molecular composition regardless of the initial static contact angle **[6].**



PBA - poly(butyl acrylate); PS - polysytrene; PBA-PS copolymer butyl acrylate - styrene;
PTFE - polytetrafluoroethylene; C, R, T - PBA-PS samples; HP - heterophase polymerization in water;
BP - bulk polymerization; SDS - sodium dodecylsulphate; PIL - poly(ionic liquid) dispersion

Fig. 5: Dependence of the rate of change of the initial water contact angle on the nature of the substrate

A New Morphology of Colloidal Particles – Multiple Suspension Particles (MSP)

A new class of colloidal polymeric particles consisting of polystyrene spheres grown in a poly (N-isopropyl acrylamide) precursor scaffold has been synthesized via redox-initiated heterophase polymerization **[7].** The morphology and thermo-responsiveness of these assemblies are proven by electron microscopy investigations and temperature-dependent measurements of the change of both the speed of sound travelling through the dispersion and the hydrodynamic particle size. Electron microscopy (EM) micrographs (transmission and scanning EM as well as cryo-scanning EM) prove the existence of colloidal clusters when the freeze-dried copolymer is redispersed in pure water **(Fig. 6).** The clusters have a size of several micrometers, contain about 800 polystyrene particles with diameter below 100 nm, and show a highly reproducible thermo-responsive behaviour with a lower critical solution temperature corresponding to that of pure poly(N-isopropyl acrylamide).

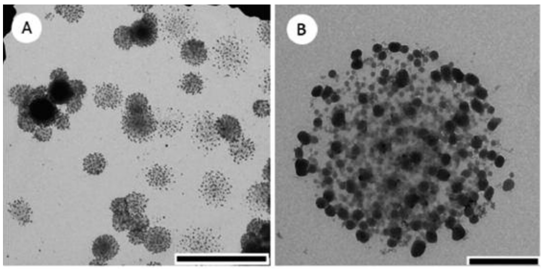


Fig. 6: TEM micrographs clarifying the particular morphology of β-CD – PNIPAM - polystyrene clusters; A – overview micrograph proving that the dispersion consists primarily of clusters and B – magnified micrograph illustrating a typical single cluster; the bars of micrograph A and B correspond to 10 and 1 μm, respectively

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Poly(ionic liquid)s as Innovative Functional Polyelectrolytes

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Poly(ionic liquid)s (PILs), also named polymerized or polymeric ionic liquids, are the polymerization products of monomeric ionic liquids (ILs) **[1].** The connection and accumulation of IL moieties through a polymeric backbone or framework builds up a macromolecular architecture featuring a high density of IL functionalities. As such, some of the unique properties and chemistry of ILs are synergistically combined with the general features of polymers, i.e. processibility, mechanical stability, chain dynamics, etc. As an extended class of conventional polyelectrolytes, numerous materials applications have been realized *via* the PILs route. This progress in turn motivates more activities in fundamental research of PILs in terms of chemical structure diversity and intrinsic structure-property-function relationship. Our group is dedicated to discovering new chemistry of PILs and studying their properties for applications in membrane technology, colloidal science, responsive materials, and carbon nanostructures.

PILs in Membrane Technology

Porous, especially nanoporous polymer membranes represent a multifunctional platform in both fundamental research and industry. In this regard, nanoporous polyelectrolyte membranes (NPMs) are particularly appealing because of the presence of charges and the high mechanical and chemical stability. However, currently no suitable fabrication method allows for large scale production of NPMs due to difficult processing associated with the water solubility and ionic feature of common polyelectrolytes. Our group introduced a facile, efficient route to achieve NPMs by exploiting electrostatic complexation between a cationic PIL and neutralized poly(acrylic acid) (PAA) **[2].** Typically, a hydrophobic, water-insoluble PIL was mixed with PAA in a 1:1 equivalent molar ratio with regard to the repeating unit **(Fig. 1).** Both were fully dissolved in DMF to form a homogeneous solution **[3].** This solution was then cast onto a glass plate, dried at 80° C, and subsequently immersed in aqueous NH3 solution. This procedure was applied to produce a large, freestanding membrane. SEM characterization proves that the 3D interconnected pores are 30-100 nm in size. Such membranes are structurally robust in various environments. Advantageously, this method produces not only traditional freestanding membranes but also functional coating. The membranes, when fabricated onto an optical fiber, serve as a highly sensitive, fast responsive fiber-optical pH sensor. This fabrication technique can be generalized to introduce pores from nano to micrometer range. When PAA is replaced by a multiacid compound, porous membranes with pore size of 0.2-3 µm were prepared, which could function as an ultrafast actuator in organic vapour **[4].**

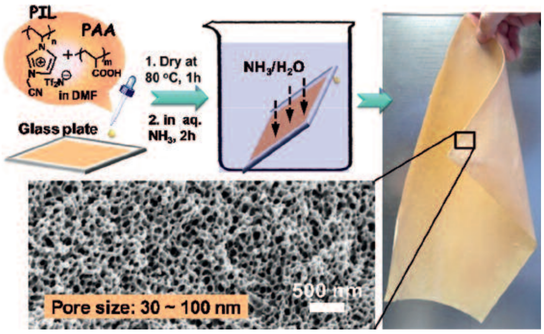

Fig. 1: Preparation scheme and a SEM image of a nanoporous polyelectrolyte membrane from a mixture solution of a cationic PIL and poly(acrylic acid) in DMF.

PILs as Stabilizer for Colloidal Systems

PILs are known as highly interfacial active materials, which bind to diverse surfaces. This function is useful for colloidal stabilization **[5].** One example is dispersion of long, slender and flexible cellulose nanofibrils (CNFs) with diameters of 5-60 nm and lengths up to several micrometers. They are a class of renewable nanomaterials with outstanding properties, such as versatile chemical-modification capacity, low thermal expansion, excellent mechanical property, and a high aspect ratio. To achieve good material performance, CNFs need to be dispersed in solution. With the assistance of PILs, we were able to disperse CNFs in solvents at will *via* grafting PIL onto CNFs **(Fig. 2).** The dispersability can be readily tuned by exchanging the counter anion. Such omnidispersable PIL/CNF hybrids served as mechanical reinforcing agent in porous membranes.

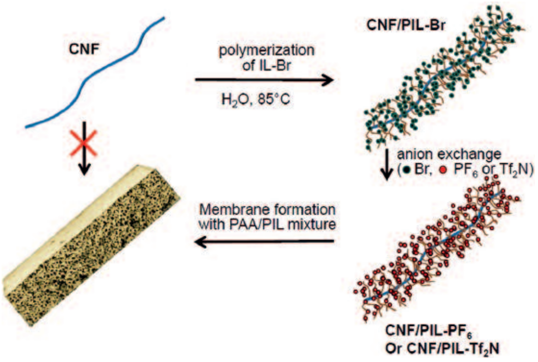

Fig. 2: Illustration of dispersion of CNFs via surface grafting of PIL onto CNFs (IL-Br: IL monomer with Br-), and the subsequent hybrid membrane preparation.

In parallel, we designed a specific PIL with a low glass transition temperature of -57°C. It exhibits a rarely observed fluidic behaviour in bulk even at room temperature (RT), different from conventional polyelectrolytes. This property enables the PIL to act as a macromolecular solvent for various compounds, and simultaneously as stabilizer for colloid particle synthesis. The synergy in the solvation and stabilization is a striking character to downsize the *in situ* formed particles **[6].**

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PILs as Thermoresponsive Polymers

Polymers with lower critical solution temperature (LCST) behaviours in solution have been widely investigated as "intelligent" materials **[7]**. However, fully-ionized polyelectrolyte homopolymers showing LCST behaviour have been ignored for a long time. We synthesized from an IL, tributyl-4-vinylbenzyl phosphonium pentanesulfonate (TVBP-C5S) the first cationic polyelectrolyte that undergoes a LCST-type phase transition in water **[8]**. Its phase transition occurs in a wide temperature range, showing dependence on polymer concentration and externally added salts. Anion exchange and salting-out effects are responsible for the flexible phase transition. Such a PIL is useful for nanoparticle stabilization and manipulation. As shown in **Fig. 3 A,** Au nanoparticles of 10 nm can be stabilized by poly(TVBP-C5S) in water at RT. Upon heating, the dispersion turns turbid due to precipitation of the poly(TVBP-C5S)-nanoparticle hybrid. Filtration through a membrane filter (0.2 µm in size) at this temperature yields a nanoparticle-free solution. Unlike conventional LCST-type polymers, the thermoresponsiveness of the hybrids can be readily abandoned by adding NaCl. NaCl addition replaces sulphate by Cl^-, which shifts the transition temperature above 100°C. By this PIL, the thermoresponsiveness of gold nanoparticles in water can be rendered or cancelled at will. In addition, we also developed the first LCST-type polyelectrolytes from a Gemini dicationic IL **[9]**.

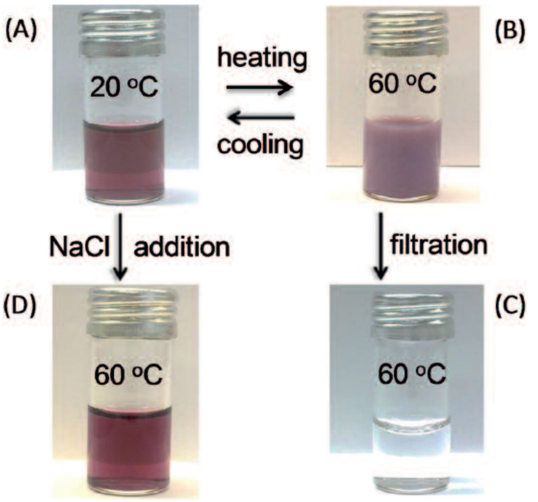

Fig. 3: Photographs of poly(TVBP-C5S) stabilized Au nanoparticles at (A) 20 °C, (B) 60 °C, (C) 60 °C after filtration, and (D) 60 °C in the presence of 0.2 M NaCl.

PILs as Carbon Precursor

Nitrogen doping of carbon nanostructures can improve the catalytic activity, oxidation resistance and electric conductivity. Recently, hollow carbon nanospheres, named "carbon nanobubbles" are one of the most intensively studied structures because of their intrinsic properties associated with the unique shape, such as high surface-to-volume ratio, high thermal and chemical stability, compartmentalized structure, and low apparent density. We have focused on this specific structure in the last two years. As example, PIL nanoparticles were used as precursor and colloidal template to create ultra-small carbon nanobubbles (25-90 nm) with controlled dimension, variable nitrogen doping, superior aqueous dispersability, high conductivity, and a distinctive atomic graphitic order **[10-11]**. In a typical synthetic route (**Fig. 4**), silica nanocasting was conducted by dropwise addition of tetramethyl orthosilicate (TMOS) into an aqueous dispersion of PIL nanoparticles under vigorous stirring. In this way individual PIL nanoparticles were initially coated with a silica layer, and eventually trapped in compact silica. Pyrolysis of the PIL/silica hybrid at 1000° C under N_2 atmosphere *in situ* converts the PIL nanoparticles into isolated carbon nanobubbles. Subsequent removal of silica releases the carbon nanobubbles into aqueous solution. Uniquely the PIL nanoparticles played a triple role as a sacrificial template, carbon precursor and N source.

Besides using PIL nanoparticles as template, an alternative way to prepare hollow carbon spheres is to graft PIL chains onto the surface of silica nanoparticles, followed by carbonization and silica etching **[12]**. These nanobubbles were successfully applied in catalysis and electrochemistry (lithium ion batteries, oxygen reduction reaction in fuel cells), and served as inorganic stabilizers for carbon nanotubes. **[10, 12, 13]**.

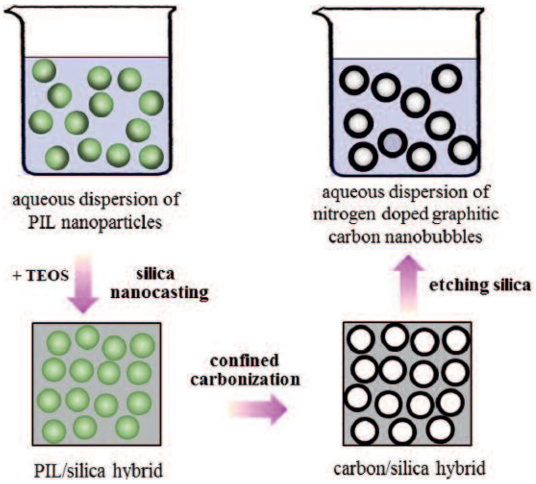

Fig. 4: Synthetic route to nitrogen-doped hollow carbon nanospheres via silica nanocasting technology through the PIL nanoparticles

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