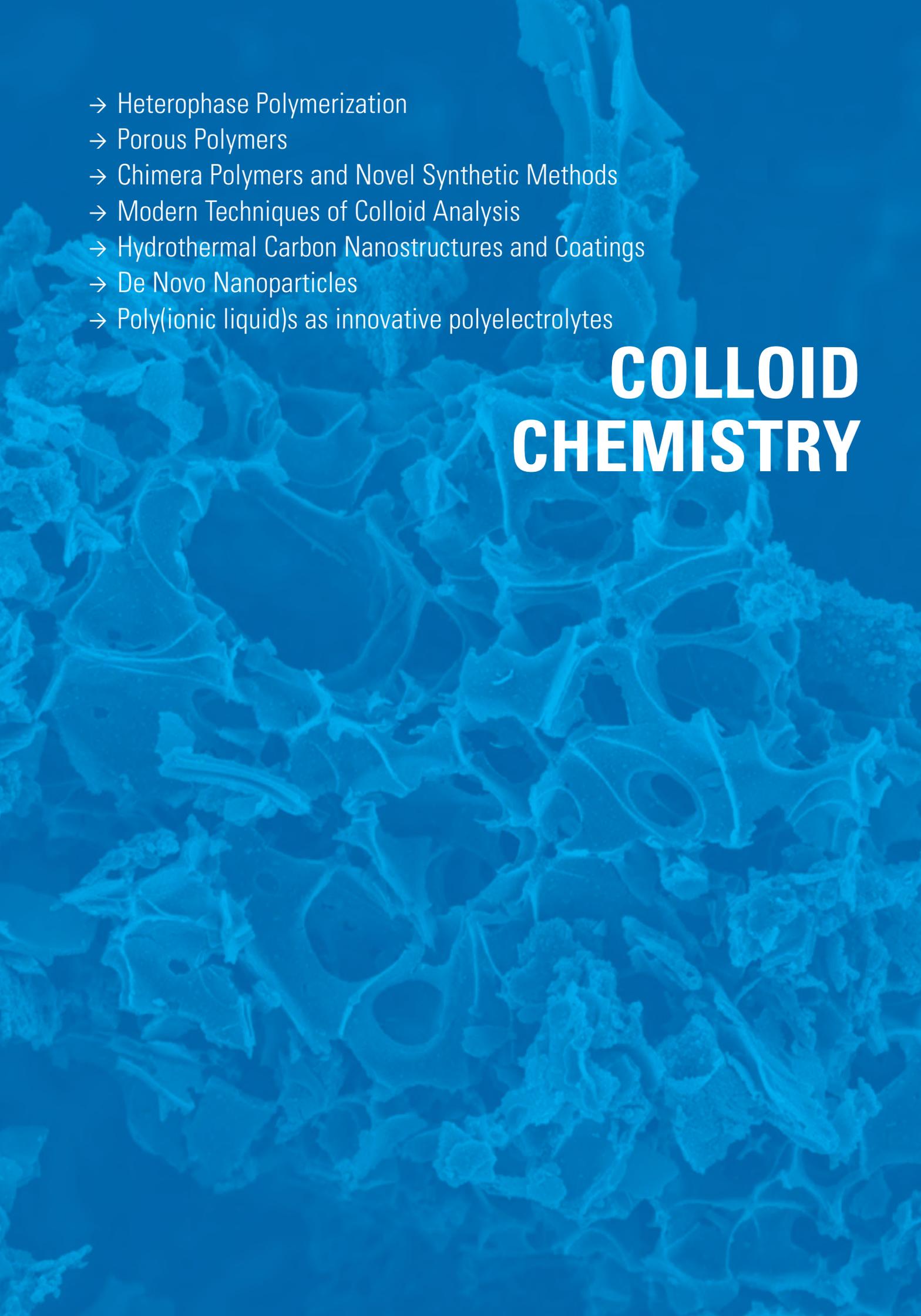


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- Heterophase Polymerization
 - Porous Polymers
 - Chimera Polymers and Novel Synthetic Methods
 - Modern Techniques of Colloid Analysis
 - Hydrothermal Carbon Nanostructures and Coatings
 - De Novo Nanoparticles
 - Poly(ionic liquid)s as innovative polyelectrolytes

COLLOID CHEMISTRY

Research in the Department of Colloid Chemistry



Scientific Profile

The overall size of the Department of Colloid Chemistry is about 65 people, covering a wide range of research topics. The effective constituting element of the scientific activities is the “project”, a structure headed by a senior scientist involving a mixture of technicians, graduate students and post-docs (3–8 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 these schemes, serious changes of my department already observed in the last two reporting periods continued to take place. Dr. Magdalena Titirici, group leader on “Sustainable Carbon”, accepted a position at Queen Mary University London, and the move of Prof. Dr. Xinchen Wang to Fuzhou University was completed, moving “Artificial Photosynthesis” into an International Joint Research Lab. At the same time, I hired Dr. Jiayin Yuan (“Polymer Ionic Liquids”, PILs), Dr. Filipe Vilela (“Photocatalysis”), Dr. Dariya Dontsova (“Photosynthesis”), Dr. Davide Esposito (“Processes for the raw material change”), and Dr. Tim Fellinger (“Electrocatalysis”) as new group leaders to start to establish their own research profile. It is fair to say that a majority of the group is now still in the primary phase of higher academic profiling, making the following report more idea that publication 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 been seriously reoriented, keeping only some of the old strongholds. The following topics are now found within the department:

- Heterophase Polymerization
- Chimera Polymers and Novel Polymerization Techniques
- Polymeric Ionic Liquids
- Service Lab Electron microscopy
- Carbon Materials and Hybrids for Energy applications
- Processes for the Raw Material Change
- De Novo Inorganic Nanostructures
- Photocatalysis and Artificial Photosynthesis

The projects below those headers are briefly explained:

Heterophase Polymerization

The notation „Heterophase Polymerization“ summarizes the techniques of suspension-, emulsion-, mini-, and microemulsion-polymerization as well as precipitation polymerization. The solvent is usually water, but heterophase polymerization in inverse media is also examined. 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. Solvent free coatings, glues, paper and fabric production are just a small excerpt of a long list where polymer dispersions have opened new possibilities and technologies, omnipresent in daily life, but usually unseen to the public.

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

- We want to simplify the 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, one-step synthesis of reinforced materials) by a rational use of the particle interfaces in heterophase polymerization (*Dr. Klaus Tauer*).
- We use new stabilizer systems (such as PILs) to generate new latexes structures and films with switchable Hydrophobicity (*Dr. Klaus Tauer, with Dr. Jiayin Yuan*)
- Emulsions stability can be accomplished even without molecular stabilizers using ultraclean conditions. The mechanisms of this process are analyzed (*Dr. Klaus Tauer*)

Chimera Polymers and Novel Polymerization Techniques

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 blockcopolymers polymers 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. Helmut Schlaad*).
- The introduction of secondary interactions such as H-bridges or dipole interactions results in superstructures with more complex order and broken symmetry, which oint the way to general rules of biomimetic mesoscale organization (*Dr. Helmut Schlaad*)

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)

Polymeric Ionic Liquids

Polymerized ionic liquids or poly (ionic liquid)s (PILs) are usually synthesized by polymerization of ionic liquid (IL) monomers and constitute a subclass of polyelectrolyte that combines a part of IL's properties with the common features of polymers. PILs are not only another class of ordinary polyelectrolytes, but carry extra properties, which can be attributed to the high polarizability of the monomer units. As such, PILs hold some unique structural merits and are advantageous in a multitude of materials applications, such as gas separation/absorption, carbon preparation, energy conversion, catalysis, and many more. PILs are also surface-active and multifunctional polyelectrolytes. Though the originally designed task of PILs was only to effectively stabilize a wide variety of diverse nanoparticles, their unexpected versatile powers were quickly recognized and contribute significant to create science from the products.

- PILs with special stabilization behavior and switchable solution properties are constructed from a wider range on organic cations and anions (*Dr. Jiayin Yuan*).
- Biodegradable and biomass-based PILs are built from hydrothermal reforming chemicals (*Dr. Jiayin Yuan, Dr. Davide Esposito*)
- PILs are used via complexation and/or carbonization as mesoporous membrane materials with high chemical selectivity and permeation (*Dr. Jiayin Yuan, Markus Antonietti*).

Service Lab on Electron Microscopy

All the work described above is necessarily accompanied by a considerable amount of colloid analysis which includes special techniques of transmission and scanning electron microscopy on soft, structured matter which are runned on the base of a central service group (*Dr. Jürgen Hartmann*).

It is a big problem that due to the financial crisis of the Max Planck Society and the delay of starting the extension building this group has to work under increasingly worsening working conditions, keeping the operations alive with constant repair of now 20 years old machines.

Materials for Energy applications

Following the former project house ENERCHEM which was devoted to materials chemistry to handle energy problems, we still work on better fuel cells, new energy cycles, new catalysts for more efficient processes, methane activation, better batteries, ultracapacitors, decentral energy storage devices. The new activities based in Golm include:

- New C/N-polymers and carbon materials to expand the property profile of carbon (*Markus Antonietti*)

- Porous polymers as membranes for fuel cells and battery separators and as novel gas storage materials (*Dr. Jens Weber*)

- Metal free catalysis and Nitride Catalysis for water splitting, methane and ammonia activation, or CO₂-reactions (*Prof. Dr. Xinchun Wang* in the international joint laboratory, new group leader *Dr. Dariya Dontsova*)

- New engineering carbons based on ILs and salt templating as electrodes and electrode membranes for fuel cells and electrocatalysis; this also includes work on supercapacitors. Another application are metal free carbon catalysts for O₂ and H₂ activation (*Dr. Tim Fellingner*)

Processes for the Raw Material Change

Hydrothermal Carbonization is a 100 year old technique to generate carbonaceous materials from biomass in a colloidal heterophase reaction processes. We reactivated in the last 10 years this process to address questions of the sustainable/chemical synthesis of carbon nanostructures and – just recently – also organic compounds. First experiments indicate that not only the non-oil based raw material base ("sugar") is highly attractive. It is also the broad range of chemistry which can be addressed and which makes this approach attractive.

- Analysis of the elemental chemical steps of HTC and hybridization with technical monomers to generate new materials, such as mesoporous scaffolds for catalysis, battery applications and modern chromatography These activities are reported, but are transferred to London with the former group leader *Dr. Maria Magdalena Titirici*)

- Performing hydrothermal processing under distinct catalytic conditions does not lead only to carbon materials, but also to valuable organic intermediates and platform chemicals. We currently focus on lactid acid generation (for bioplastics), the synthesis of ionic liquids from biomass in water and the production and valorization of a rather clean lignin fraction (*Dr. Davide Esposito*)

De Novo Nanoparticles

Many materials, which are relevant for novel energy cycles and more efficient chemical reactions (catalysis) do not exist 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 metal carbide and nitride nanostructures, which offer new options for metal/base catalysis, but also are record holders in mechanical hardness and magnetization. In general, both size and shape add to the demanded properties and must be controlled or adjusted. (*Dr. Cristina Giordano*)

- Based on paper as a reactant and printing of metal salts, we expect to develop a simple access to functional catalytic arrays and electrodes via materials transcription (*Dr. Cristina Giordano*)
- Unconventional heating devices such a focused light, microwaves, or induction coupling enables unconventional solid state processes with extreme temperature ramps and unmatched reaction control. This is explored for nanoparticle synthesis in salt melts (*Dr. Tristan Corbiere*)
- 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. Xinchun Wang, Dr. Dariya Dontsova*).
- Metal doped C_3N_4 has turned out to be a valuable catalyst for a number of oxidation, photoreduction and photocoupling reactions (*Markus Antonietti, Dr. Dariya Dontsova, together with UNICAT/ TU Berlin*)

Photocatalysis Artificial photosynthesis

The international joint laboratory on Artificial Photosynthesis was established in July 2008 between the Max-Planck Institute of Colloids and Interfaces (Prof. Markus Antonietti) and Fuzhou University (Prof. Xianzhi Fu). The lab is now lead by Prof. Dr. Xinchun Wang, a former MPI group leader. The 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, are both in the center of this program. An important challenge in artificial photosynthesis is the development of antenna structures or light converters 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 band-gap. 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.

- The search for appropriate nanoscopic co-catalysts for oxygen liberation or CO_2 conversion is another key issue. Here we work on new carbon structures, cobalt oxides as well as on metal carbides and metal nitrides (*Markus Antonietti, Dr. Cristina Giordano*)
- The melon principle was recently generalized by polymerizing special conjugated microporous polymers (CMPs) with a special design which also allows working in direct contact with oxygen and water. These polymers are now used for polymer photocatalysis, for instance for continuous singlet oxygen generation (together with the *Seeberger* department) or other oxidative rearrangement reactions (*Dr. Filipe Vilela*)

Visions and Future Perspectives for the Next Years

The special situation with a change of overall 75% of the group leader positions promoted a recent redefinition and reorientation of the department. After a temporal phase of being too much involved in taking care of too many independent Junior careers, I personally prefer to enter a period with more coordinated research and longer term goals focussed around as director and more tightly bound junior people.

Our trials to cooperate with the National Excellence Centre on Catalysis of the TU Berlin have not only led to an exchange of staff, but are to my opinion very promising, concerning the development of completely new catalytic schemes (with TU Organic and Inorganic Chemistry) There are some high impact schemes with TU Berlin in the pipeline.

The started 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. IN addition, the donation of the ERC Advanced Excellence Award has already led to some very promising co-operations and broken paradigms. It is my intention to expand these activities by further focussing and profiling.

Larger Equipment and Central Service Labs of the Department

Commercial standard techniques which are available in the department are:

- transmission and scanning electron microscopy,
- static and dynamic light scattering,
- diverse techniques of light microscopy,
- a chromatographic lab including a number of modern chromatography techniques,
- reaction calorimetry with online multidetection,
- analytical and preparative ultracentrifugation,
- thermal analysis, DSC and porosimetry,
- MALDI-TOF-mass spectrometry,
- FT-ATIR for liquid analysis.

One of the labs, the electron microscopy lab, is a so-called "central service labs", i.e. it belongs and is operated by the department, but is also designated to perform scientific routine measurements for the whole institute.

All other instrumental labs are not devoted to service operations, but are nevertheless heavily involved in inter-department projects.

Relations to Industry and Society

The department is involved in a large number of industrial projects. We promote fruitful and truly mutual relations with BASF AG and Firmenich. These operations include scientific cooperation, knowledge exchange, consulting, the solution of minor scientific problems or measurements, and knowledge transfer to create the scientific base for products of the companies.

I am a board member of 15 scientific journals, and I consult the Royal Society of Chemistry/UK in questions of international exchange and benchmarking. I am the Sekretar (chair) of Natural Sciences of the Berlin-Brandenburgische Akademie der Wissenschaften. In science policy, I regularly act as a referee in DFG, European and International science evaluations. I am in the Advisory Board of both the Thailand and the Brazil Centers of Nanotechnology. I regularly go to schools and lecture about the problems of a developing society and how to respond on the base of scientific knowledge and education.

Markus Antonietti
Director of the Department
of Colloid Chemistry

Polymer Dispersions/Heterophase Polymerizations



Colloidal processes are omnipresent in the chemical industry and particularly in polymer chemistry, heterophase polymerization is a centennial technology which nowadays produces high-tech polymeric materials with a value of several billion euros per year [1]. Thus, better understanding of heterophase polymerization and educating students on this topic is of general scientific and economic interest.

Klaus Tauer 27.09.1951

1974: Diploma, Chemistry
(Friedrich-Schiller University Jena)
Thesis: Dye Sensitization of

Photoconductivity of
Poly(arylene vinylene) Polymers

1978: PhD, Polymer Chemistry
(Friedrich-Schiller University Jena)
Thesis: Investigations of spectral

sensitization of photoconductivity
of poly(arylene vinylene) polymers

1977-1991: Scientific Coworker
Institute of Polymer Chemistry of
the Academy of Sciences of
the GDR in Teltow-Seehof

Since 1992: Group Leader
(Max Planck Institute of Colloids
and Interfaces, Potsdam)

Since 2004: "Privatdozent" Polymer
Colloids, University of Potsdam

Schizomorphic Latex Particles

"Schizomorphic" particles, prepared by special radical heterophase polymerization techniques [2], possess the ability to change shape and morphology in dependence on the particle concentration. At very low concentrations, the particles even disintegrate from spheres into rods, rings, and webs [3] (Fig. 1). Hence, for amphiphilic block copolymer particles, conclusion regarding morphology and shape in the dispersed state, based on normal SEM or TEM images, should be made extremely cautiously.

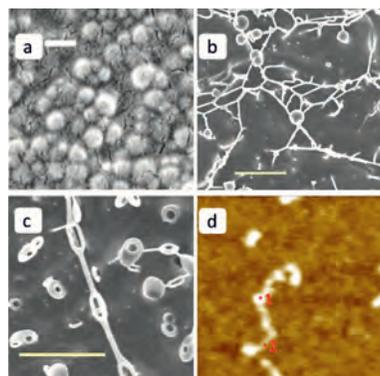


Fig. 1 Different morphologies observed for amphiphilic polystyrene-co-poly(styrene sulfonate) particles; a – SEM micrograph, dry sample from 0.4 %, bar 200 nm; b, – cryo-SEM micrograph, 0.4, bar 500 nm; c – AFM image from 0.0004%, side 400 nm (1 – 1.344 nm, 2 – 0.556 nm)

Photo-Initiated Bulk and Emulsion Polymerization

A comparative experimental study of bulk and emulsion polymerization of styrene with bis-(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (BAPO) or bis-(4-methoxy benzoyl)-diethylgermanium (BAG) as photoinitiator or photoinitiator-free reveals astonishing similarities and anticipated differences [4]. Photopolymerization of styrene with initiation in the monomer phase is under homogeneous and heterogeneous conditions as bulk and emulsion polymerization, respectively, characterized by essentially the same features with respect to radical formation and chain growth. In either case the polymerization can be started photochemically with normal fluorescence tubes as light source which are also used for indoor illumination.

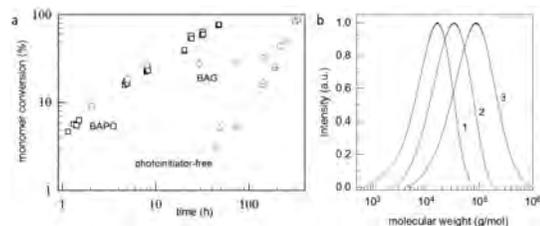


Fig. 2 a - Correlation between monomer conversion and polymerization time for photo-initiated bulk polymerization of styrene; b - Development of the molecular weight distributions (BAPO): 1 – 4, 2 – 22, 3 – 76 % conversion

The bulk polymerizations in the presence of photoinitiators continue even after complete decomposition of BAG and BAPO without the effect of dead end polymerization is being observed (Fig. 2a). For BAPO initiated polymerization this is the expected behaviour as photodecomposition of phosphine oxide chain ends entails continuous generation of initiating radicals [5, 6]. For BAG this effect seems less pronounced but nevertheless the bulk polymerization goes on for more than 100 hours after complete photoinitiator consumption, interestingly, with increasing rate as also observed for the photoinitiator-free polymerization over the entire duration.

The average molecular weight increases, independent of the polymerization procedure and recipe, with monomer conversion suggesting a certain kind of 'photo-controlled' chain growth (Fig. 2b).

Taken all experimental results together, we suggest that a photo electron transfer reaction between a styrene monomer and a repeating unit in the polystyrene chain leads repetitively to generation of radicals (actually radical ions) ensuring both polymerization in the absence of photoinitiator and increasing molecular weight with conversion [4].

Influence of Gas Phase Composition on Heterophase Polymerization

The outcome of radical styrene heterophase polymerization depends strongly on the composition of the gas phase. Experimental data show that the effect of the gas phase is quite a complex one and strongly influenced by the nature of the gas, the homogeneity or heterogeneity of the polymerization system, and the kind of initiator [7].

Evidence has been found that the influence of air goes beyond the simple action of oxygen which can cause deceleration or acceleration of the reaction. The experimental results show that the optimum polymerization conditions are obtained in the absence of any foreign gas. The connection between the preceding discussion and heterophase polymerization is given by the colloidal nature of these systems and the experimental fact that the rate of polymerization and the rate of degradation of the emulsion show essentially the same dependence on the composition of the gas phase.

Poly(Ionic Liquids) as Stabilizers in Emulsion Polymerization

Poly(ionic liquid) (PIL) nanoparticles were for the first time applied as sole stabilizers in aqueous emulsion polymerization and revealed an astonishing and unexpected behaviour [8]. In a well-dispersed state, the PIL nanoparticles serve as an unexpectedly effective stabilizer for polystyrene dispersion, enabling solids content of greater than 40 %. However, the same PIL as dry powder is hydrophobic and, in accordance with Bancroft's rule, unable to stabilize aqueous dispersions. The ambivalent behaviour of PIL is extremely beneficial for the application of aqueous dispersions because, as desired for decades, the hydrophilic dispersed state during synthesis turns hydrophobic in the dried state during application of the polymer. This conclusion is supported by contact angle measurements on corresponding polymer films made of dried latexes (Fig. 3). Water shows on polystyrene made with sodium dodecylbenzenesulfonate as a typical common hydrophilic stabilizer a contact angle of $82.1 \pm 2.1^\circ$. The contact angle for polystyrene made with PIL stabilizer is significantly larger ($95.3 \pm 1^\circ$).

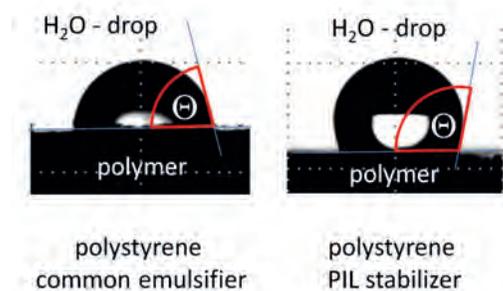


Fig. 3 Contact angle of water drops on polystyrene films illustrating the different hydrophobicity

Plant Cell Models via Polymerization

Plants adapt the geometry of their organs and tissue properties to cope with external and internal stresses and to actuate organ movement. These actuating movements function without an active metabolism, but are humidity-based systems where a swellable material acts against a stiffer cell wall. Within this project we explore the possibility to mimic the mechanical behaviour of papaya plants.

Within the SPP1420 we explored possibilities to build a humidity-sensitive actuator following the principles used by the papaya plant [9]. We mimicked the papaya cell walls by radical copolymerization in a shape-similar PTFE-template (Fig. 4 a and b). A suitable polymerization recipe comprises butyl acrylate (BA) with either glycidyl methacrylate (GMA) or hydroxyethyl methacrylate (HEMA) as comonomer (molar ratio BA:comonomer of 4:1) and 1 mol% of ethylene glycol dimethacrylate as crosslinker to avoid phase separation. The polymerization was started photochemically with BAPO (UV LED as light source) at room temperature. The parenchyma hydrogel was mimicked by subsequent polymerization of a mixture acrylic acid/methylene bisacrylamide inside the cells of the polymer grid (Fig. 4c). Initiating this polymerization with

the ceric ion redox systems leads to covalent attachment of the hydrogel to the cell walls.

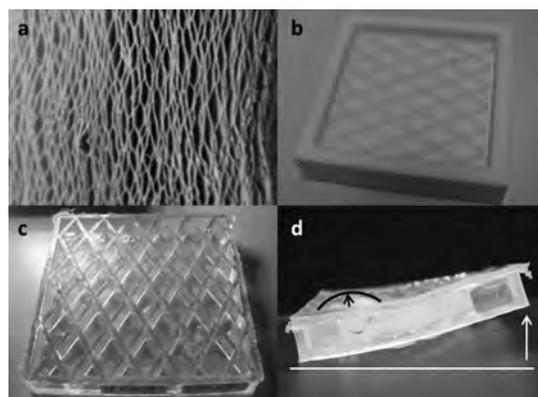


Fig. 4 a – Phloem cells of papaya plants; b – Teflon template for the production of the polymer grid; c- Artificial cells mimicking papaya phloem before filling certain cells with hydrogel via radical polymerization; d – Self-lifting of the artificial grid by swelling of the hydrogel inside selected cells of the grid proving the principle of a humidity-sensitive actuator

Due to the confinement of the hydrogel inside the cell, during swelling mechanical distortion of both the filled cells and the whole assembly of cells (Fig. 4d) happens.

Amphiphilic Block Copolymer Particle

Heterophase polymerization is a simple but powerful tool for the synthesis of special block copolymer particles. Particularly interesting is the synthesis of particles for potential biomedical applications such as pullulan decorated poly(hydroxyethyl methacrylate) particles.

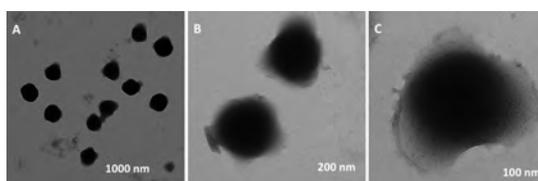


Fig. 5 Transmission electron micrographs of pullulan-g-PHEMA graft copolymer particles

Both homopolymers are biocompatible and have already been successfully used in medical applications for decades. We reported their combination in nano-particles (Fig. 5) for the first time [10].

In another study a new class of amphiphilic particles with a very special morphology has been discovered when the block copolymer synthesis is carried out in the presence of cyclic sugars [11].

K. Tauer, K. Krüger, P. Höhne, N. Weber, S. Purkayastha, R. Yu, U. Lubahn, S. Pirok, I. Shekova; in collaboration with Y. Yagci (Istanbul Technical University), J. Hartmann (electron microscopy, MPI KGF), J. Yuan (MPI KGF); klaus.tauer@mpikg.mpg.de.

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- [11] R. Yu, K. Tauer, in preparation,

From Polymer Synthesis to Porosity Analysis



Jens Weber 17.05.1981

2005: Diploma, Chemistry

(Technische Universität Dresden)

Topic: Physical Chemistry of Ionic-

Nonionic Comb Terpolymers

2007: PhD, Polymer & Colloid Chemistry

(MPI of Colloids and Interfaces, Potsdam)

Thesis: Meso- and Microporous High

Performance Polymers

2008-2009: Postdoc, (Arrhenius Labora-

tory, Stockholm University, Sweden,

with Prof. Lennart Bergström)

Since 2009: Project Leader – Porous

Polymers (MPI of Colloids and

Interfaces, Potsdam)

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on the Observable Porosity in Intrinsical-

ly Microporous Polymers, *Macromolecu-*

les 2011, **44**, 1763-1767

Porous polymers represent a flourishing area of research, which is driven by both: academic and industrial interest. Porous polymers are relevant in a number of applications ranging from thermal insulation, gas separation or storage, catalysis to separation technologies. The group is interested in new synthetic methods and advanced characterization of nano-

porous polymers, namely micro- and mesoporous polymers. Interaction with guests (including gas separation) as well as dynamic processes and stimuli-responsiveness of the nanoporous structures are among the core interests of the research unit.

Microporous polymers, i.e. polymers having pore sizes of less than 2 nm can be considered as the polymer analogue of zeolites and activated carbon and combine very high specific surface areas ($>>100 \text{ m}^2\text{g}^{-1}$) with the rich synthetic possibilities of polymer science.

Mesoporous materials have pore sizes between 2 and 50 nm. They are of interest in separation technologies, especially for larger (bio)macromolecules. However, their science is less explored compared to microporous polymers.

Sustainable Monomers and Methods

Recently, microporous polyesters and polyurethanes were synthesized from a renewable natural resource, betulin (**Fig. 1**). Betulin is the main component of the birch bark and hence not in conflict with food production. Its content can be as high as 30 wt.-% and it is easily extractable by common organic solvents.

Betulin was used as a rigid monomer to synthesize polyester and polyurethane networks with intrinsic microporosity, **[1,2]** which are made from up to 75 wt.-% of renewable materials. The stiff structure of betulin prevents close packing of the polymer chains.

Betulin can also serve as a monomer for linear, soluble polymers, which can be cast into self-supporting membranes. The obtained materials show promising results for CO₂ over N₂ selectivity and might indeed be useful as gas separation membranes **[1]**.

Next to microporous materials, betulin can also be used as the hydrophobic constituent of amphiphilic multiblock copolymers (with *Helmut Schlaad*) **[3]**.

Sustainability can also be achieved by reaction control. Replacing organic solvents by water is a promising concept and was expanded to the synthesis of fully aromatic polyimides **[4]**. The details of this new reaction are under investigation and initial steps towards morphology control of the resulting high-performance polymers could also be achieved.

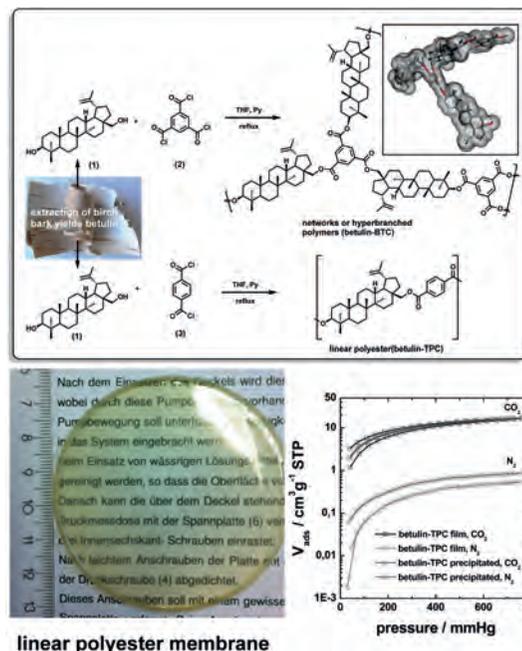


Fig. 1: chemical structure of cross-linked and soluble betulin-based polyesters, photograph of the free-standing membrane and typical gas adsorption isotherms at 273K.

Microporous Soluble Polymers

The first chiral microporous polyimides have been synthesized using a binaphthalene-based monomer. The resulting polymers showed a significant surface area, but the pores were apparently too small to allow access of larger organic molecules. The homochirality was lost upon polycondensation (partial racemisation) and no superstructure formation could be observed yet **[5]**.

Next to the synthesis of new polymers of intrinsic microporosity, interest was spent to a better understanding of the microporosity (free-volume). The influence of intermolecular interactions on the observable porosity could be proven. Hydrogen bonding can lead to pore size reductions, which can also be reversed upon temperature increase, i.e. the breaking of hydrogen bonds **[6]**.

Conjugated Microporous Polymers

Conjugated microporous polymers (CMPs) are a subclass of microporous polymer networks and are built from (fully) conjugated monomers.

The functionalization of arylene-ethynyle type CMPs by radical thiol-yne chemistry was demonstrated. The concept allows the on-demand functionalization of CMPs with functional groups **[7]**.

A contrary concept is the use of copolymerization methods in order to tune the optical bandgap of CMPs. Introducing thiophene units into a spirobifluorene-based system could shift the emission color from blue to green. Additionally, it could be shown that energy transfer from the CMP to incorporated guest molecules is possible [8].

The formation of a photoactive CMP based on the acid-base responsive phenolphthalein without affecting the switching ability was demonstrated [9]. The final network can be switched between two different states (small pores, ionic charges vs. larger pores, neutral state). The porosity and the polarity (as probed by the heat of carbon dioxide adsorption) of the material could be tuned depending on the counterions (Li^+ vs. Cs^+) (Fig. 2).

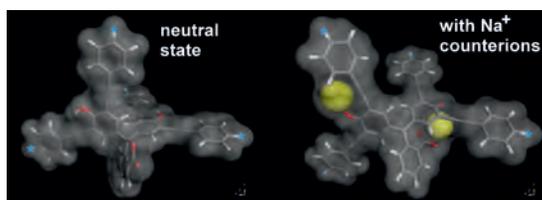


Fig. 2: 3D representation of the central motif of the phenolphthalein CMPs in the neutral and charged state. Blue stars indicate connection points. Please note the changes of the geometry (fixed coordinate systems) upon switching and the influence of the counterion (yellow) size.

Mesoporous Polymers

Mesoporous polymers can be synthesized either using templating methods or by controlled phase-separation processes. We employed hard-templating of spherical silica nanoparticles for the synthesis of mesoporous polymers.

A general problem of the hard-templating routine is the often-observed immiscibility of the aqueous silica nanoparticle dispersions with the organic monomers, which leads to phase separation. Acidified melamine-formaldehyde resin precursors could however be mixed homogeneously with the aqueous dispersion due to favorable electrostatic interactions. The dispersion could be cured to yield mesoporous hybrid materials (as a consequence of phase-separation processes), whose porosity could even be enhanced by removal of the silica [10]. The resulting porous resins showed promising behavior for gas separation applications as well as good properties for heavy metal ion removal. The low-price and scalability of the method make those materials indeed interesting for relevant technologies.

Another way to overcome the miscibility problem is to process the nanoparticle dispersion into a monolithic structure. This was achieved by an evaporative method, which resulted in monoliths made of mainly random-close packed (RCP) nanoparticles. Backfilling of the interstitial voids with liquid monomers (e.g. divinyl benzene, DVB) and subsequent polymerization yielded highly porous polymers after template removal [11]. The porosity ϕ of the polymers is directly related to the space-filling of the RCP phase (typically $\phi \sim 64\%$). The spherical mesopores have only a low polydispersity and their size

is related to the size of the used nanoparticles (~ 12 or ~ 25 nm). Specific surface areas of up to $1000 \text{ m}^2\text{g}^{-1}$ could be achieved and post-functionalization (e.g. sulfonation) of the pores is possible without loss of the porosity.

Mesoporous polymers prepared in such way are hence ideal model systems (uniform pore size) for the study of the mesopore collapse phenomenon, which is not yet understood. To elucidate the structural changes upon drying, the drying process of the solvent-filled polymers was followed by small-angle X-ray scattering (SAXS, in-house and at BESSY) (Fig. 3). It was shown that the pores undergo drastic deformation (even in the fully cross-linked state) before the solvent actually evaporates. This can be understood as a consequence of the different forces (elastic, interfacial) involved in the process. The finer details are subject to ongoing analysis.

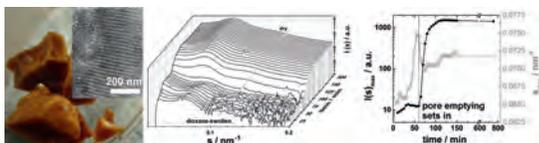


Fig. 3: left-hand side: photograph of sulfonated mesoporous PolyDVB, inset: respective TEM micrograph; middle: in-situ SAXS patterns (drying process of dioxane filled poly(DVB) with 12 nm pores); right-hand side: intensity (black) and s -value (grey) of the peak vs. time. The drastic change of s_{max} (which relates to $> 10\%$) before the pore emptying sets in is obvious.

The hard-templating pathway was also extended to other monomer systems. Ionic liquid type monomers based on vinyl imidazolium were used in cooperation with the group of Jiayin Yuan [12]. The so-called poly(ionic liquids) are discussed as materials with potential for CO_2 separation and the impact of the mesostructure on the adsorption properties were studied. A significantly faster and higher adsorption was found, which can be attributed to the significantly shorter diffusion pathways. Beside the kinetic facts, there are some peculiarities related to the adsorption thermodynamics and the state of the adsorbed CO_2 , which require additional analysis.

Porosity Characterization

The expertise of the group in the characterization of microporous materials by various methods has also led to a number of cooperation projects with various partners. The main tools are nitrogen and carbon dioxide adsorption studies and the use of X-ray scattering, which can give additional information, even on disordered materials.

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Smart Biohybrid Polymers



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Bioconjugates and biohybrid copolymers are interesting materials for the generation of "smart" functional colloids and hierarchical structures, for usage in for instance life science applications (targeted drug delivery, tissue engineering, etc.). New materials based on amino acids, sugars, and terpenes have been prepared by advanced polymer synthesis techniques and studied according to their stimuli-responsive behavior and hierarchical self-assembly in aqueous environment or in solid state.

Synthesis

Metal-free "living" ring-opening polymerization of heterocycles and photochemical thiol-ene/yne click modification [1] were applied to prepare terpene-poly(ethylene oxide) (PEO) copolymers (Fig. 1a) [9], glycopolypeptides [16] and -peptoids (Fig. 1b) [11]. Glycosylation of unsaturated polypeptides could be achieved under experimentally mild and benign conditions, i.e. in aqueous media at room temperature.

Well-defined poly(2-oxazoline) (pseudo-polypeptide) star ionomers were readily synthesized by photo thiol-yne functionalization/crosslinking of block copolymer micelles in water (Fig. 1c) [3].

Polymer brushes on inorganic substrates (gold surfaces and glass fibers) were prepared by the thiol-initiated photopolymerization of vinyl monomers [7, 12].

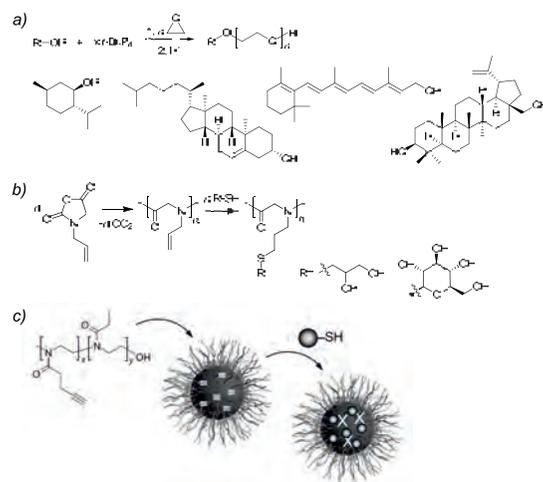


Fig. 1: Synthetic routes to biohybrid and pseudo-polypeptide polymers

Stimuli-Responsive (Smart) Polymers

Secondary structures of statistical copolypeptides of L-glutamate and glucosylated L-/DL-allyl- or DL-propargylglycine were studied in dependence of solution pH. The glucosylated and non-glucosylated samples adopted random coil conformation at neutral-basic media and α -helical conformation in acidic media, the helical content depending on the number and configuration of allyl-/propargylglycine units. The glycopolypeptides revealed enhanced helical stability and solubility down to pH 3.5 (Fig. 2). Furthermore, turbidity assays

demonstrated selective binding to the plant lectin concanavalin A [16].

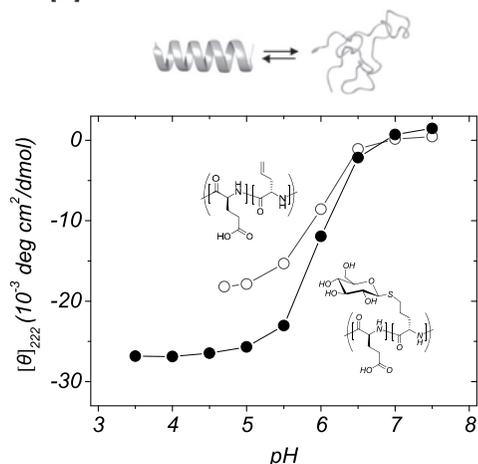


Fig. 2: pH-dependent secondary structures (helix-coil) of poly(L-glutamate) copolymers in water.

Cholesteryl-PEO and betulinyl-(PEO)₂ amphiphiles showed thermo-responsive aggregation behavior in water. The polymers precipitated or coagulated upon heating, due to the dehydration of PEO chains, and re-dispersed upon cooling. Furthermore, betulinyl-(PEO)₂ with short PEO chains (11 repeat units) showed dual thermo-responsive behavior, precipitating at high temperature and turning into hydrogel at low temperature (Fig. 3). Results suggested that the solution behavior was controlled by the type of terpene and polymer architecture [13].

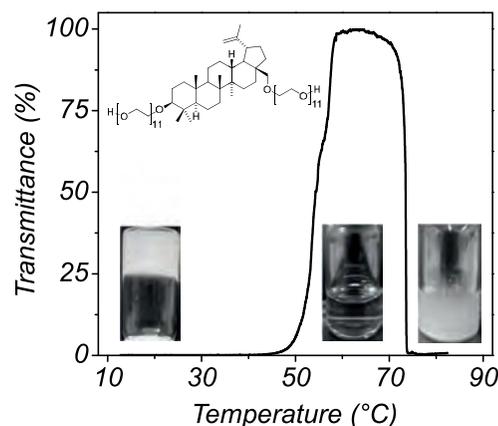


Fig. 3: Dual thermo-responsive solution behavior of a betulinyl-(PEO)₂ amphiphile at 5 wt% in water.

The thermo-responsive behaviors of poly(2-ethyl-2-oxazoline) star ionomers in water were studied according to effects of pH, ionic strength, and type of salt. The cloud point temperatures varied in a wide temperature range, from 10 to >95 °C, corresponding with the Hofmeister salt series and ionization degree of the core (Fig. 4). Effects of pH were weakened by the addition of salt, however, kosmotropic salts (Na₂SO₄) being more effective than chaotropic salts (NaSCN). For star

MODERN TECHNIQUES OF COLLOID ANALYSIS

Electron Microscopic Studies of Colloidal Systems and Interfaces



The investigation of structure/property relationships and chemical synthesis/structure relationships of both natural and synthetic colloidal materials and interfaces is important for the development of new materials for analytical and technical applications. Transmission electron microscopy and high-resolution scanning electron microscopy are suitable techniques to investigate micro- and nano-structured synthetic organic and inorganic particles, active coatings and interfaces, membranes, composite materials and naturally-grown biomaterials. The determination of structural parameters such as the size and size distribution of colloidal particle systems, the pore size of polymeric and inorganic networks, the diameter of fibrillar nanostructures, the spatial arrangement of particles are in focus on the electron microscopic investigations. In combination with energy-dispersive X-ray spectroscopy scanning electron microscopy is a powerful analytical tool to determine relationships between the local chemical composition and surface and interface structures of solid materials. Because of the organisation of the institute, there are many closed cooperations between the electron microscopy group and other research groups. Some of the interesting results of electron microscopic investigations are presented here.

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and naturally-grown biomaterials. The determination of structural parameters such as the size and size distribution of colloidal particle systems, the pore size of polymeric and inorganic networks, the diameter of fibrillar nanostructures, the spatial arrangement of particles are in focus on the electron microscopic investigations. In combination with energy-dispersive X-ray spectroscopy scanning electron microscopy is a powerful analytical tool to determine relationships between the local chemical composition and surface and interface structures of solid materials. Because of the organisation of the institute, there are many closed cooperations between the electron microscopy group and other research groups. Some of the interesting results of electron microscopic investigations are presented here.

Iron oxide nanoparticles have a relatively low magnetic saturation and metallic iron has a much higher saturation magnetization, but is unsuitable for medical applications due to its toxicity. An alternative, offering both high magnetic saturation and chemical stability, is iron carbide (Fe_3C) [1]. By dispersing an aqueous iron precursor within gelatine gel, it could show that the polymer controls the nucleation of magnetite nanoparticles within the gel matrix. The biopolymer decomposes to form a carbon- and nitrogen-rich matrix around the intermediary oxide nanoparticles. This reactive template then induces carbothermal reduction of iron oxide to iron carbide. As an example for the general applicability of this method two biopolymers (chitosan and alginate) were used as gel components to produce stable iron carbide nanoparticles in the range of 10 to 30 nm [1]. The high-resolution scanning electron microscopic results show that the iron carbide nanoparticles were embedded in an amorphous matrix (Fig. 1).

Elemental analysis showed over a half of the mass to be composed of carbon (27 wt.%) and nitrogen (28 wt.%), suggesting that the amorphous matrix was formed from decomposition products of the gelatine starting material. The particle structure was confirmed using transmission electron microscopy and the mean particle diameter calculated to be $d = 20 \pm 2$ nm.

Another interesting project is the electron microscopic characterization of the structure of Pickering emulsions. For the preparation of a stable oil in water emulsion the solid nanoparticles should be able to wet the oil, as well as the water phase.

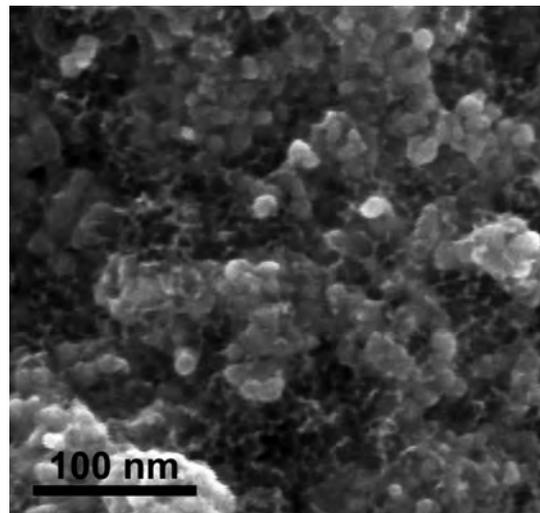


Fig. 1: Iron carbide nanoparticles synthesized using iron acetate in ammonium alginate precursor gel.

Therefore the surface chemistry of the particles must be manipulated in a proper way [2]. Here the polyacid poly(methacrylic acid sodium salt) and the polybase poly(allylamine hydrochloride) are used for the surface modification of oppositely charged alumina and silica colloids.

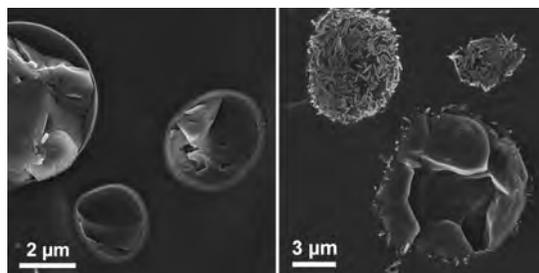


Fig. 2: Dodecane droplets with silica-PAH nanoparticles (left) and Hexadecane droplets stabilized by halloysite (aluminosilicate) nanotubes (right)

Using high-resolution cryo-scanning electron microscopy the sample preparation takes place at very low temperatures (<173 K) and the aqueous and the oil phases are in solid state. The modified solid colloids are covering the oil phase completely and stabilizing the emulsion droplets (Fig. 2).

An important project is the local modification surface structure of soft matter with laser light. Here we have investigated a method of incorporating laser responsive heat centers, gold nanoparticles, into flake like microparticles assembled from fullerene derivative [3]. The samples were prepared by centrifugation of gold nanoparticle together with fullerene derivative based microparticles. Fig. 3a is representing the morphology of the hybrid material where gold nanoparticles

are embedded in the flakes of the microparticle. Upon laser irradiation at 532 nm, the hybrid microparticle melts due to plasmonic heating of gold nanoparticles and the flower-like microparticle will smoothen the surface (Fig. 3b), which lead to a loss of hydrophobicity. Although in principle, fullerene derivative absorb light at 532 nm and could lead to a melting, it is suffice to mention that at intensity used here the melting does not occur (Fig. 4).

The incorporation of laser responsive agents, can be used to selectively modify the morphology and the physical properties of the microparticles.

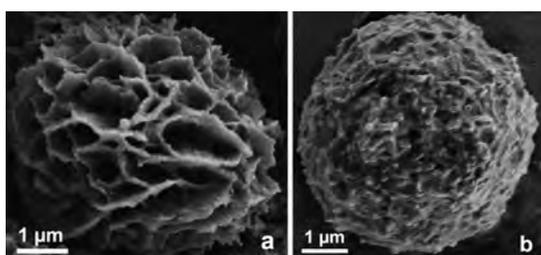


Fig.3: Gold nanoparticle embedded on flakes of fullerene derivative based microparticles (a) before and (b) after laser treatment.

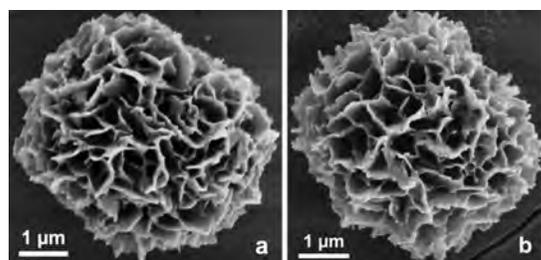


Fig.4: Stable flower-like microparticles without Au-nanoparticles (a) before and (b) after laser treatment.

One of our research activities is focused in the development of a coating system, including a non-chromate conversion coating layer and a self-priming top coating containing non-toxic corrosion inhibiting components for high-strength aluminum alloys [4]. Moreover, the presence of some alloying elements such as copper and surface defects particularly increases pitting corrosion attack by forming galvanic couples. To detect the surface defects and spatial distribution of the alloying elements scanning electron microscopy in combination with energy-dispersive X-ray spectroscopy was used.

Fig. 5 shows the surface morphology (a) and the partial phase separated structure of a polished uncoated aluminum alloy (b), where the matrix is rich in aluminium (coloured in teal) and the red coloured areas are rich in copper. The mixed colours of the elemental map represent the local composition. The mean composition of the matrix contain 93.2 wt.% Al, 1.4 wt.% Mg and 4.8 wt.% Cu (Fig. 6 teal spectrum) whereas the local areas rich in copper contains up to 50 wt.% Cu (Fig. 6 red spectrum).

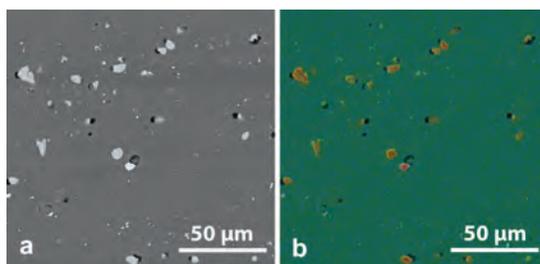


Fig.5: Surface morphology of the polished uncoated aluminum alloy (a) and the corresponding elemental map (b).

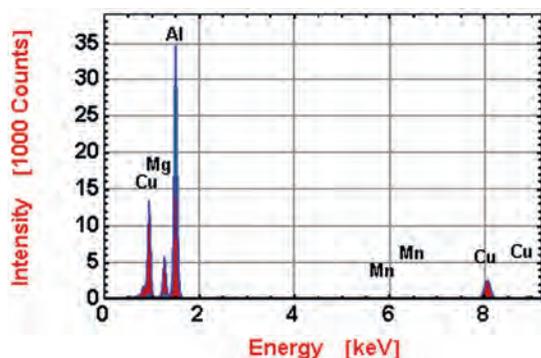


Fig.6: EDS-spectra of the uncoated aluminium alloy

The dark gray area in Fig. 5a corresponds to the aluminium matrix and the bright areas are rich in copper.

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Carbon Materials from Renewable Resources



Introduction

Porous carbon materials are becoming of increasing interest to the developing application fields of energy storage [1] (e.g. electrodes for Li ion batteries or supercapacitors), fuel cells (e.g. novel catalysts or catalyst supports for the oxygen reduction reaction) [2] or chromatography technologies. [3]

With the development of modern technology and the need of better preforming materials, a larger number of new carbon materials with well-defined nanostructures have been synthesised by various physical and chemical processes, such as fullerenes, carbon nanotubes (CNTs), graphitic onions, carbon coils, carbon fibers, and others. To date, it is probably fair to say that researches on carbon materials are encountering the most rapid development period.

Despite its wide spreading and naturally occurrence on Earth, carbon has been mainly synthesised from fossil based precursors. Pressures of an evolving sustainable society are encouraging and developing awareness amongst the materials science community of a need to introduce and develop novel porous media technology in the most benign, resource efficient manner possible. Carbon has been created from biomass from the very beginning throughout the process of coal formation. Nature is mastering the production of carbons from biomass and we only need to translate it into a synthetic process.

Hydrothermal Carbonisation (HTC)

HTC is not a new concept, but was first introduced by Bergius in 1913 who described the transformation of cellulose into coal-like materials.[4] However, while the Bergius process was based on the liquefaction of coal for the production of biofuels, our research focus is the carbonisation of biomass for the production of functional porous carbon materials.[5]

HTC is a fascinating field of research, with much about it developed in the past seven years [6] but far more to be discovered. In simple terms, it is a mimic of natural coalification on a timescale of hours rather than millions of years.[5a, 5c, 7] We recently added another piece of mechanistic understanding.[8] The term “functional carbon” inherently implies some sort of function, i.e. applicability of the material. Below I will give a few examples of sustainable synthesis of porous materials and their applications.

Emulsion Templated Macroporous Carbons as Electrodes for Enzymatic Biofuel Cells

We have designed carbon monoliths using an easy synthetic pathway based on High Internal Phase Emulsion (HIPE) as a soft-template to confine the polymerisation-hydrothermal carbonisation of both saccharide derivatives and phenolic compounds. After further thermal treatment under inert atmosphere, the as-synthesised macroporous “Carbo-HIPES” feature interesting mechanical properties, together with high electrical conductivity up to 300 S.m⁻¹. Moreover, these new conductive foams exhibit a hierarchical structure, associated with the presence of macro, meso- and micropores, leading to specific BET surface areas and DFT total pore volumes up to 730 m².g⁻¹ and 0.313 cm³.g⁻¹ respectively. In view of attractive structural characteristics and intrinsic properties, these macroporous monoliths have been incorporated within electrochemical devices, as modified thin carbon disc electrodes. After immobilisation of glucose oxidase-based biocatalytic mixture, a promising improvement of the catalytic current density by a factor 2 compared to commercial glassy carbon electrodes was observed towards electro-oxidation of glucose.

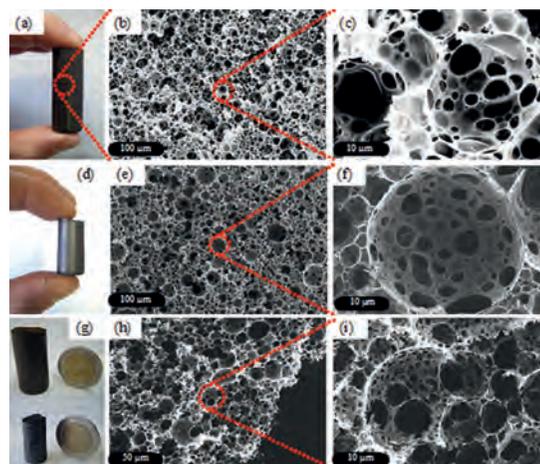


Fig. 1: First row: HTC-CarboHIPES after Soxhlet extraction and drying at 80 °C; Second row: CarboHIPES after further thermal treatment at 950 °C; [9]

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Hydrothermal Carbon-based Nanostructured Hollow Spheres (HS) as Electrode Materials for High-Power Lithium-Sulfur Batteries

For addressing efficient, cheap and sustainable energy storage devices, lithium-sulfur batteries (LSBs) are one of the most promising candidates for next-generation rechargeable storage devices. Indeed, while sulfur is an affordable and abundant element, its light weight leads to high theoretical specific capacity and energy density. A number of researches on cathode materials for LSBs have been carried out in the last decade. Composites made of sulfur and porous carbon have been shown to significantly improve both energy densities and cycling abilities. We focused herein on the synthesis of nanostructured carbons through the hydrothermal carbonisation of biomass-derived precursors, according to an eco-efficient and cost-effective synthetic route. We synthesized porous carbon hollow spheres (HSs) exhibiting ~80 nm internal diameters and less than 10 nm thick nanostructured shells. We have compared 3 different materials as positive electrodes in Li-S batteries: 1. hollow carbon spheres/S composites prepared by S melt diffusion; 2. hollow carbon spheres/S composites prepared by a simple mixture; 3. non-porous carbon spheres mixed with S. A fine control of the shell thickness and porosity allowed a simultaneous optimisation in the achieved specific powers, specific energies and cycling properties of the carbon-sulfur composite electrodes. The best results were obtained when using the hollow spheres infiltrated with S by melt diffusion (discharge capacity of 1000 mAh.g⁻¹ at the 1st cycle, maintains a discharge capacity of 600 mAh.g⁻¹ at the 50th cycle). Even at a very high current density of 10C (=16750 mA.g⁻¹), our cathode showed a discharge capacity of 170 mAh.g⁻¹. If we assume that a full Li-S cell using HS contains 25 wt.% of Li₂S, this full cell will provide a specific energy of 460 Wh.kg⁻¹ and a specific power of 5000 W.kg⁻¹.

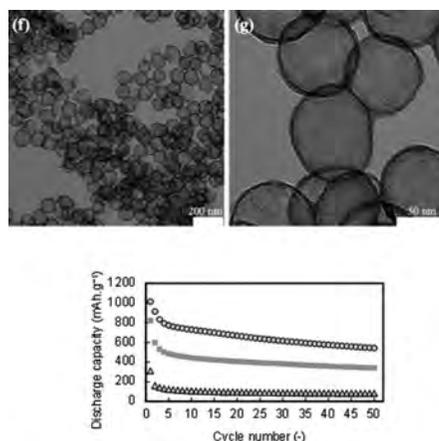


Fig. 2: Carbon-based HS. The cycling stability of the composite made by melt diffusion method is indicated by circles. The cycling performance of the mixture of HS and S is indicated by squares, while the one associated with the mixture of HTC non-hollow microspheres and S is indicated by triangles.

Sulfur and Nitrogen Doped Carbon Aerogels with Enhanced Electrocatalytic Activity in the Oxygen Reduction Reaction

We have developed one-pot, hydrothermal synthesis of nitrogen and sulfur dual doped carbon aerogels. Two comonomers, S-(2-thienyl)-L-cysteine (TC) and 2-thienyl carboxaldehyde (TCA), were used for sulfur incorporation, while the nitrogen was provided by a gelating protein, i.e. ovalbumin. [10] This approach gave rise to distinct morphologies and varying doping levels of sulfur. Nitrogen-doping levels of 5 wt% and sulfur-doping levels of 1 wt% (using TCA) to 4 wt% (using TC) were obtained. A secondary pyrolysis

step was used to further tune the carbon aerogel conductivity and heteroatom binding states. By comparing solely nitrogen-doped with nitrogen- and sulfur-doped carbon aerogels, it was observed that the presence of sulfur improves the overall electrocatalytic activity of the carbon material in both basic and acidic media.

Other few examples from our research include the development of cellulose [11] or rye-straw [12]-based porous electrodes in Lithium ion batteries, efficient CO₂ adsorbents from algae [13] as well as upgrade of bio-wastes remaining from the production of bio-ethanol into electrodes for supercapacitors. [14]

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Novel Synthetic Routes for Nanoparticles Production



Introduction

Ceramic materials are largely present in our everyday life in many different fields, from (bio)medicine to electronics, catalysis, photocatalysis, etc. Metal nitrides (MN) and metal carbides (MC) are a special class of ceramics with features extending oxides. Together with excellent mechanical properties and chemical stability MN/MC possess electrical conductivity and catalytic activity, which place them –function-wise – between ordinary ceramics and pure metals. Despite this high potential, the use of MN/MC is still comparably limited, mainly due to synthesis limitations. Classical approaches require in fact very high temperatures, toxic precursors or complicated multi-step processes. In the last few years, in our group alternative pathways have been designed, also allowing shaping and processing and several MN/MC nanoparticles and nanostructures have been produced for targeted applications in a sustainable way [1].

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Nanoparticles for Energy Applications

In a word in constant evolution, scientists have the delicate issue to provide suitable materials to fulfill the contemporary necessities. This is especially important in energy related matter, where valid alternatives to the current systems must still be found. Also here, despite the wide range of possibilities, the attention is still mainly devoted to some selected classes of materials, while MN/MC could provide a valid alternative to other well-establish systems (metals and noble metals for instance). In order to produce a variety of MN/MC structures in a sustainable way, a sol-gel-type process was set up using suitable N/C sources (from small molecules like urea to polymers like gelatine), which also act as stabilizing agents. The attention was focused on energy related materials, particularly interesting for classical and novel catalytic processes (VN, MoC, WC, etc), photocatalysis and photovoltaics (TaON, $Zn_{1.7}GeN_{1.8}O$ and GaN@InN), electrochemistry and battery applications (e.g. $Fe_3C@C$, $MnN@C$).

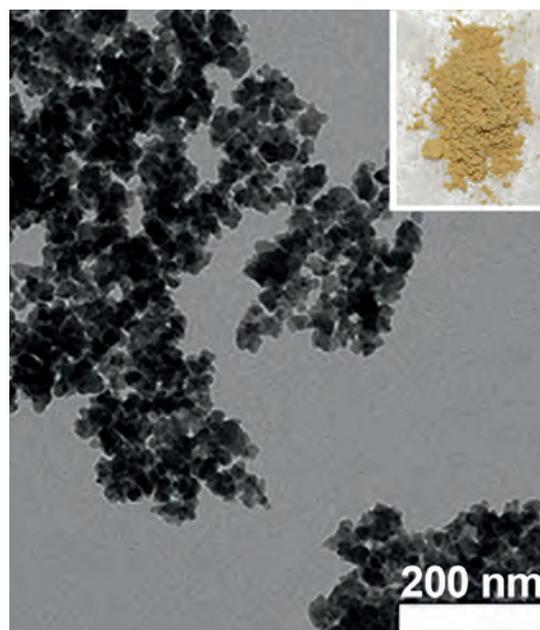


Fig.1: TEM picture of $Zn_{1.7}GeN_{1.8}O$ nanoparticles, in the inset the corresponding powder sample [2]

From Paper to Carbon Electrodes by Printing

Bio-structures display a high degree of complexity and can be used to bring features such as porosity, high surface area and complex design into a final ceramic material. With this aim, a simple synthesis toward hierarchical microstructures of magnetic iron carbide (Fe_3C) starting from pure cellulose was designed. In this study, ordinary filter paper was turned into mesostructured iron carbide/graphene nano-assemblies with high structural perfection. Shape retention at the macroscopic scale was also proved by calcination of a “crane-origami” (Fig. 2) previously embedded in a Fe sol- precursor solution. In these composites the iron carbide nanoparticles add functionality, e.g. a high saturation magnetization, conductivity, filtration properties and (electro)catalytic activity, while the polymer/carbon matrix gives processability and shape.



Fig.2: An origami (paper) crane previously soaked in a suitable iron salt solution then calcined, turns in a magnetic object (and thus attracted by a rectangular magnet, left) made of small Fe_3C nanoparticles embedded in a graphitic matrix (inset, right)

Furthermore, by using the paper as a support and combining it with a catalytic ink (by ink-jet printing), functional carbon/ceramic arrays and 3D structures were produced. The process allows turning mere cellulose into mesostructured graphene nano-assemblies and can be used as the basis for further processing, for instance copper electro-deposition [3].

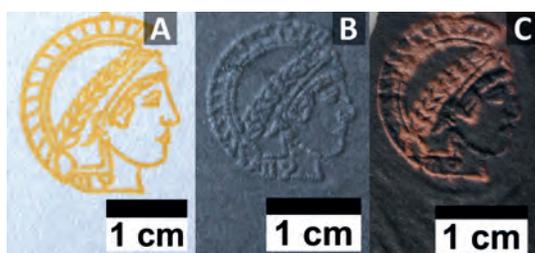


Fig. 3: A) Printed sample, B) after calcination, C) after copper deposition

Towards Hybrid Systems: $\text{Fe}_3\text{C}@\text{ILs}$

After progresses toward sustainable synthesis as pure phase, the production of MN/MC based hybrids and/or nanocomposites (by functionalization with a suitable second phase) was a further step in our research. The coupled phase can be a poly-ionic liquid (PILs) or a carbon phase, and can act as a mere dispersant but can also facilitate further processing (e.g. casting or coating) [4]. For instance, nanoparticles with magnetic properties embedded in a PIL matrix, couple the magnetic properties with the PIL characteristics [5].

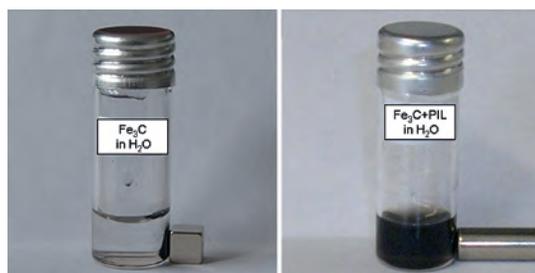


Fig.4: Fe_3C nanoparticles dispersed in water can be attracted by an external magnet, while stay stably dispersed in a PIL solution.

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Poly(ionic liquid)s: Synthesis and Materials Application



Poly(ionic liquid)s for Functional Materials

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Poly(ionic liquid)s or polymerized ionic liquids (PILs), stand for a special subclass of polyelectrolytes which connect ionic liquid (IL) moieties through a polymeric backbone to form a macromolecular architecture. In such a structural configuration, some of the unique properties of ILs are brought to the polymer chains. Meanwhile the general properties of polymers are preserved. This generates a unique type of functional polymer materials. Nowadays PILs are catching steadily increasing interest in numerous applications in a broad range, such as solid polymeric ion conductor, universal stabilizer, microwave adsorbing agents, CO₂ capture, electroactuator, etc. Our group is dedicated to making new structured PILs, and applying them as/in carbon precursor, thermoresponsive soft matters, and catalysis.

PILs as Carbon Precursor

Imidazolium- and pyridinium-based ILs have been used as valuable carbon precursor due to their negligible vapor pressure, high thermostability and abundance in heteroatoms. The advantage of PILs over ILs in the carbon production lies in the shape controllability at various length scales. PILs were previously reported to produce graphitic, mesoporous and conductive carbon nanostructures using metal salts as activation agent. In our current research activities, metal salts were excluded to hold the heteroatoms to modulate their chemical and electric properties. In one example, via electrospinning technique, nitrogen doped carbon fibers and membranes were synthesized from PILs with well-defined chemical structures (Fig. 1). In detail, vinylimidazolium or vinylpyridinium type PILs with an allyl functionality and a dicyanamide anion in each repeating unit were electrospun into fibers together with a trithiol crosslinker molecule (TRIS) and a radical initiator (ACVA). The fibers were radically crosslinked and then carbonized at 1000 °C to form nitrogen doped carbon fibers and membranes. The SEM image in Fig. 1 visualized a fiber monolayer on a silicon wafer and a freestanding carbon membrane prepared by this method. The fibers were 0.2 to 2 μm in diameter and showed a satisfactory conductivity of 200S/cm.

In another example, via layer-by-layer technique, cationic PIL poly(3-cyanomethyl-1-vinylimidazolium bromide) and an ionic polyelectrolyte poly(ammonium acrylate) as the deposition pair coated the silica particle surface uniformly. Carbonization at 1000 °C and template removal delivered carbon hollow spheres of 200 to 600 nm in size, 7.2 wt % in nitrogen content and with a high surface area of ca. 400 m²/g.

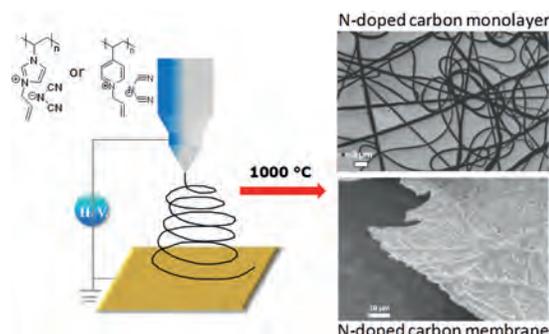


Fig. 1: Synthetic route to nitrogen-doped carbon fibers and membranes from electrospun PILs. The right side presents the SEM images of a nitrogen-doped carbon monolayer and a freestanding membrane.

PILs as Thermoresponsive Polymers

Ion responsiveness of PILs is a well-known feature. The thermal switching behavior of PILs currently catches huge attention, however less is known. We studied the low critical solution temperature (LCST) behaviour of an anionic PIL poly(4-tetrabutylphosphonium styrene sulfonate) (PTPSS). Unlike some neutral polymers like poly(N-isopropylacrylamide) (PNIPAM) with a stable transition temperature, PTPSS changes its transition temperature in a wide range upon concentration variation. Fig. 2 illustrates that the cloud point (T_{CP}) for PTPSS was 82 °C at 20 g/L, and decreased gradually to 67, 61 and 52 °C at 50, 100 and 200 g/L. In all cases, the phase transition was very sharp.

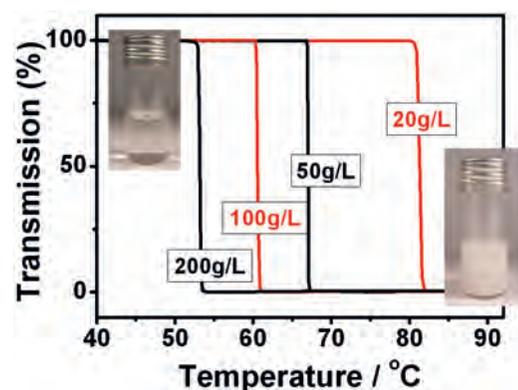


Fig. 2: Transmission vs. temperature plots of the aqueous solutions of PTPSS at different concentrations.

Foreign salts were an additional tool to modulate their solution behaviour. While KBr shifted the transition to high temperatures, tetrabutylphosphonium bromide and the monomer salt could lower it down even to room temperature. Indeed, the LCST-type phase transition of PTPSS is very unique and is dependent on the polymer concentration and external salts. PIL copolymers could show also tunable and designable LCST-like solution behavior. **Fig. 3** displayed double stimulus-responsiveness behaviour of a PIL copolymer poly(NIPAM-co-1-ethyl-3-vinylimidazolium bromide) [poly(NIPAM-co-EVImBr)] in aqueous solution. The copolymer remained stable in aqueous solution upon heating or adding KBr salt, as the other non-stimuli affected part always takes over the stabilizing role. Only the simultaneous combination of both effects could destabilize the solutions with a precisely adjustable T_{cp} in a wide temperature window by tuning the copolymer composition and the ionic strength. Such a solution behaviour was a synergistic effect of the PNIPAM fraction, a LCST-type neutral polymer with a transition temperature at 32 °C and the bromide-containing PIL, a polyelectrolyte sensitive to ionic strength. This “double key principle” could be coupled with the stabilization function of the PIL to process carbon nanotubes. By stabilizing carbon nanotubes with this type of multi-responsive copolymers, the aqueous stability of CNTs is variable over a wide temperature range.

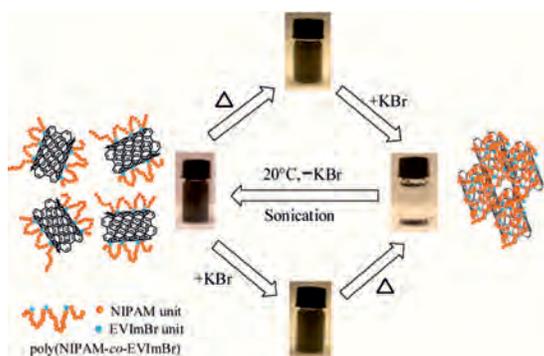


Fig. 3: Schematic Illustration of “double key switching system” to formulate a temperature and ionic strength responsive MWNT dispersion by using a poly(NIPAM-co-EVImBr) copolymer stabilizer.

PILs in Catalysis

PILs can work as catalyst, catalyst support or pre-catalyst. Our group focused in the last two years on the supporting function of PILs in catalysis. Due to the charge feature, PILs can stabilize catalytically active metal nanoparticles. For example, a spherical PIL brush system based on a crosslinked

polystyrene core and densely grafted poly(1-ethyl-3-vinylimidazolium bromide) shell could serve efficiently as support for noble metal nanoparticles, such as Pt or gold. The catalytic system based on PIL-Pt could catalyze the reduction of nitrophenol, a widely found pollutant in industrial waste water, by sodium borohydride. Furthermore, the catalytic activity of the metal nanoparticles embedded in the PIL spherical brushes was found to be modulated by externally added salt. A significant decrease in the catalytic activity was observed at high NaBr concentration.

In another system, porous interpolyelectrolyte complex nanostructures of cationic PIL and poly(acrylic acid) (PAA) were tested as catalyst support for aerobic oxidation reaction. The complex was prepared via a novel precipitation route via dropping a mixture solution of PIL and PAA in DMF into ethanolic ammonia solution (**Fig. 4**).

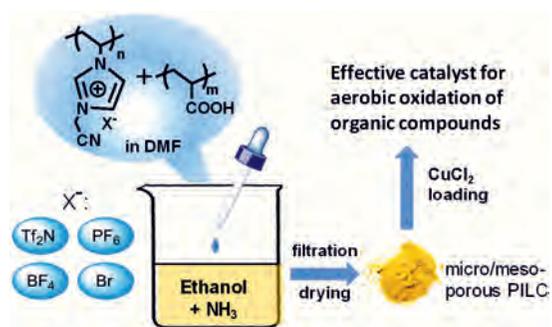


Fig. 4: Synthetic route to micro/mesoporous PIL complex based on poly(3-cyanomethyl-1-vinylimidazolium) PILs and PAA, and their application for aerobic oxidation of organic compounds.

The porous materials, termed poly(ionic liquid) complex (PILC) was precipitated out because of the *in-situ* neutralization of PAA and the corresponding complexation of PAA with poly(3-cyanomethyl-1-vinylimidazoliumbis(trifluoromethanesulfonyl)imide) in a non-aqueous medium. Nitrogen sorption measurements indicated a total specific surface area of up to 310 m²/g in these PILC materials. The PILC materials could load copper salts in an unconventional ion pair binding mode, which allowed for an uptake of 25 wt% of CuCl₂ into the PILC matrix. The resulting hybrids were used as an effective heterogeneous catalyst for the aerobic oxidation of hydrocarbons under mild conditions. Both high activity and selectivity were achieved for this catalytic system.

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NANOSTRUCTURED MATERIALS FOR ENERGY STORAGE, CONVERSION AND PHOTOCATALYSIS

Design of 3D-Conjugated Polymers as Heterogeneous Photocatalysts



Introduction

Organic conjugated oligomers and polymers are an important class of semiconductor materials, attracting great interest in applications such as organic light emitting diodes (OLEDs), photovoltaics, organic field effect transistors, electrochromic devices and sensors. Optimization of a device performance is a major challenge in this field and there is a range of electronic and structural features that can be manipulated to improve a material's suitability towards a particular device. The design and construction of an ideal material for organic semiconductor devices requires careful consideration of a range of physical properties. Conjugated microporous polymers (CMPs) offer the same advantages of conventional conjugated polymers, with extended π -systems where the electronic levels can be controlled rendering materials that are semiconducting and have a wealth of applications. Furthermore, and given the distinct morphological properties of CMPs, (including porosity and high surface areas) π -conjugated microporous materials have been gaining more and more attention recently. CMPs have been widely studied in areas such as gas separation and storage, taking advantage of their high surface areas and porosity. More recently, conjugated polymer networks are making their way into catalytic systems as heterogeneous catalysts.

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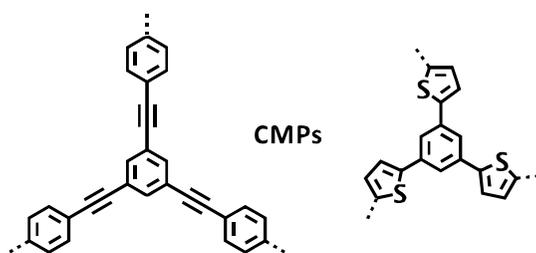
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Self-Assembling Conjugated Macromolecules for Organic Field Effect Transistors and Solar Cells

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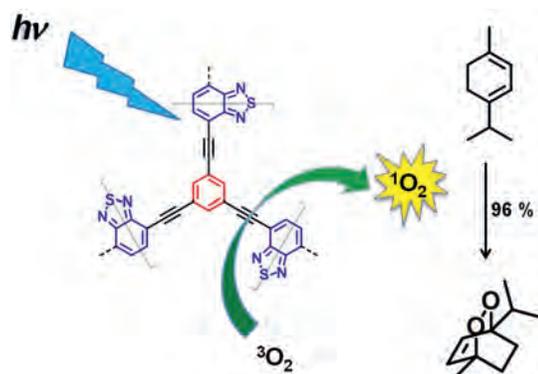
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Conjugated Microporous Polymers for Heterogeneous Photocatalysis



The general concept of our research is to develop novel photoactive conjugated polymer networks, (CMPs) with a high level of control over their electronic and structural properties for application in Heterogeneous Photocatalysis, an important technology in solar energy conversion and sustainable chemistry.

Background

Having established the potential for photoinduced charge transfer of a CMP to an acceptor molecule, it is valid to assume that this class of materials has the potential to act as heterogeneous photocatalysts (on their own merit) and/or as metal catalyst supports (again heterogeneous). Indeed, our current research in this field has made some notable breakthroughs where a novel CMP synthesized has shown to be able to act as a photosensitizer in the production of singlet oxygen for ene type reactions. This poses a major advancement as current photosensitizers are generally dissolved in the reaction media and once the reaction is completed the desired product is obtained via costly and cumbersome separation techniques in order to remove the catalyst. With the CMP, a simple filtration is sufficient to remove it from the reaction media and this heterogeneous photocatalyst can be readily reused without significant loss of its catalytic activity.



Singlet oxygen generation via photoactivation of benzthiadiazole bearing CMP for conversion of α -terpinene into ascaridole

Methodology

In the first instance, and employing the CMPs synthesized according to knowledge already gathered, heterogeneous photocatalytic reactions (including: singlet oxygen activation, trifluoromethylations, CO₂ reduction and water-splitting) are attempted solar light simulators as source of photons to excite the polymer network at room temperature (the absence of heat represents a major advantage over other common catalytic systems and is in line with sustainability). The reasoning behind the choice of the reaction will be determined by the energetic levels, (HOMO and LUMO), of the CMPs that meet the requirements for a particular reaction. Also, and once the structural factors that determine the photocatalytic activity have been identified, novel CMPs will be synthesized accordingly. Synthesis and characterization of novel CMPs with a high level of control of their morphological properties is also fundamental for a high performing heterogeneous catalysis. Surface area, pore size and pore volume (including pore connectivity and percolation within the material) influence the interfacial level where the catalytic event takes place. Synthesizing CMPs in the presence of silica nanoparticles (for instance) can provide a useful method to template the polymeric material, increase its surface area and achieve defined pore size once the template is removed. Synthetic post-modification of the CMPs can also help control surface

area and introduce new features that include water compatibility of the CMP and coordination sites to metal nanoparticles (application of photocatalytic reactions in water and in the absence of volatile organic compounds, VOCs, is again in line with sustainable and green chemistry). Also, metal nanoparticles can be incorporated into the polymer voids in order to enhance and access different photocatalytic reactions. Ultimately, and having achieved important milestones, such as control of electronic and morphological properties of the CMPs; ensure the chemical stability of the polymer framework during photocatalysis; incorporation of inexpensive and abundant metal nanoparticles within the porous materials; photocatalyze organic reactions in polar solvents and water and in the absence of VOCs; the aim will be to develop a material (or combination of materials) that can catalyze economical and sustainable reactions which replace traditional and expensive metals (palladium, ruthenium, iridium, etc.) such as in carbon-carbon formation, epoxidation of olefins, CO₂ reduction and water-splitting directly using solar light as the source of photons.

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