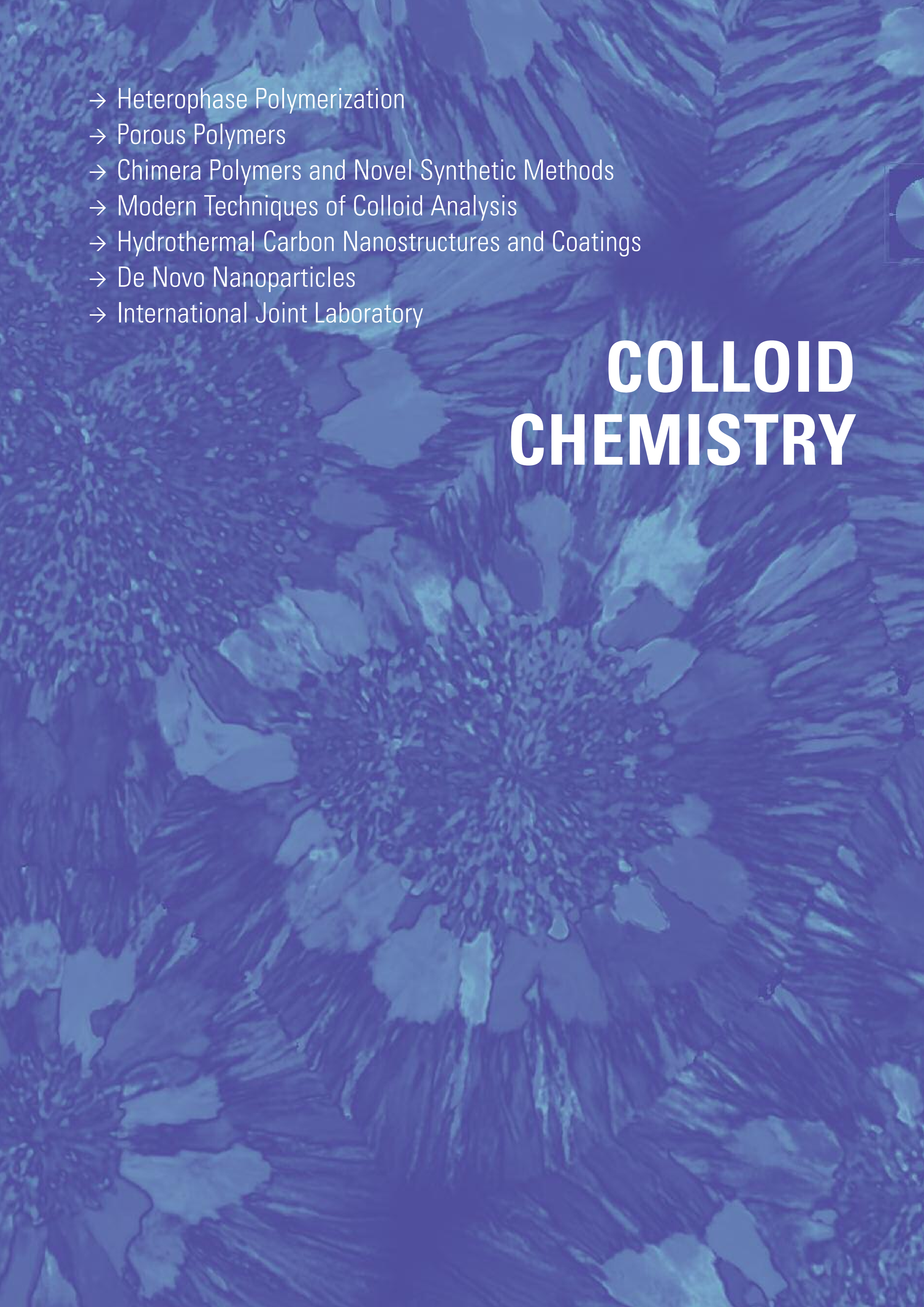


- → Heterophase Polymerization
- → Porous Polymers
- → Chimera Polymers and Novel Synthetic Methods
- → Modern Techniques of Colloid Analysis
- → Hydrothermal Carbon Nanostructures and Coatings
- → De Novo Nanoparticles
- → International Joint Laboratory

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 size of the Department of Colloid Chemistry is currently about 60 people, with independent researchers covering a wide range of research topics. The effective constituting element of the scientific activities is the "project", 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 have a temporal character of usually about 5 years. After this time, permanent scientists 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 former group.

In the time of this report and after a further "drain" of 2 group leaders in the period ahead, reconstruction of the department went on and was most serious. Dr. Helmut Cölfen, left for Full professorship to the University of Konstanz, and the Emmy Noether group of Dr. Hans Börner now turned into a Full Professorship at the HU Berlin. This was followed by the leaving of a set of key Post-Docs towards permanent international positions, which complemented the drain. The just recently established groups of Dr. Maria Magdalena Titirici on "Hydrothermal Carbon", Dr. Cristina Giordano ("De Novo Nanoparticles"), and Dr. Xinchen Wang ("Artificial Photosynthesis") are now complemented by another two fresh group leader, Dr. Jens Weber ("Porous Polymers") and Dr. Jiayin Yuan (Polymeric Ionic Liquids, starting from 2011). This turnover is beyond typical and not 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 treated by the department:

· Heterophase Polymerization
· Chimera Polymers and Novel Polymerization Techniques
· Modern Techniques of Colloid Analysis
· Materials for Energy applications
· Hydrothermal Carbon Nanostructures and Coating
· New inorganic nanostructures
· Artificial photosynthesis

These projects within these project groups 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. The solvent is usually water, but heterophase polymerization in inverse media is also examined. This class of techniques, although more than 90 years old, experiences a strong renaissance, since it allows the production of high polymer containing formulations in water as an environment-friendly solvent.

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

· We want to gain a better understanding of the nucleation period and particle formation for an optimal control of the particle size and polydispersity. For this purpose, new experimental online multidetection techniques are developed; the experimental investigations are supplemented by theoretical and numerical descriptions *(Dr. Klaus Tauer)*.

· 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, foams) by a rational use of the particle interfaces in heterophase polymerization *(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. Recently, we learned that very special effects, not only for biological interfaces, can be addressed when one block is a biopolymer, whereas the other mediates to the "technical world" (Chimera Polymers). Focal points of interest in this range are:

· The micelle formation and lyotropic liquid crystalline phase behavior of chimera 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, dipole interactions or metal-ligand binding results in superstructures with more complex order and broken symmetry *(Dr. Helmut Schlaad)*.
. A new organization principle based on two immiscible, both water soluble blocks was identified. These double hydrophilic block copolymers enable the separation and self organization of two aqueous entities *(Dr. Helmut Schlaad, with Markus Antonietti)*
· The performance of molecular drugs or diagnostic particles can be highly enhanced or optimized by coupling to a colloidal system with synergistic action. Here, our specific knowledge on the synthesis and physical behavior of functional polymers and nanoparticles is used in cooperation with pharmaceutical/medical partners to generate tailor made colloidal diagnostica *(Dr. Cristina Giordano, together with the Seeberger department)*.

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 data handling. The developments in this area include special techniques of transmission and scanning electron microscopy on soft, structured matter *(Dr. Jürgen Hartmann)*.

Due to the promotion of some of the previous group leaders, headhunting of young scientists in area is requested to keep the analytical strength also within the department. This however is an ongoing operation.

Materials for Energy Applications

The Max Planck Society has established a new instrument to improve the impact and visibility of basic science for society, so-called project clusters or project houses. The first of these project houses to come into existence was ENERCHEM, devoted to the materials chemistry to handle energy problems. This project house was initiated by the Inorganic Chemistry Department of the Fritz Haber Institute and the Colloid Chemistry Department and is coordinated by Markus Antonietti.

Hydrogen storage, better fuel cells, new energy cycles, new catalysts for more efficient processes, methane activation, better batteries, ultracapacitors, 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, especially in electrocatalysis and fuel cell applicaitons *(Dr. Jiayin Yuan, Markus Antonietti)*

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

Hydrothermal Carbon Nanostructures and Processes

Hydrothermal Carbonization is a 100 year old technique to generate carbonaceous materials from biomass in a colloidal heterophase reaction processes. We reactivated this process to address questions of the sustainable/chemical synthesis of carbon nanostructures and the climate change. First experiments indicate that not only the non-oil based raw material base ("sugar") is highly attractive; it is also that a multiplicity of useful carbon nanostructures can be addresses with great ease and high potential:

- HTC of raw biomass to generate soil conditioner ("black soil") and its interaction with the microbial biosystem *(Markus Antonietti, Maria Magdalena Titirici, together with the MPI of Biogeochemistry)*

- Analysis of the elemental chemical steps of HTC and hybridization with technical monomers to generate new filler structures *(Dr. Maria Magdalena Titirici)*

- HTC reaction to coat nanoparticles and mesoporous scaffolds for catalysis, battery applications and modern chromatography *(Dr. Maria Magdalena Titirici)*.

De Novo Nanoparticles

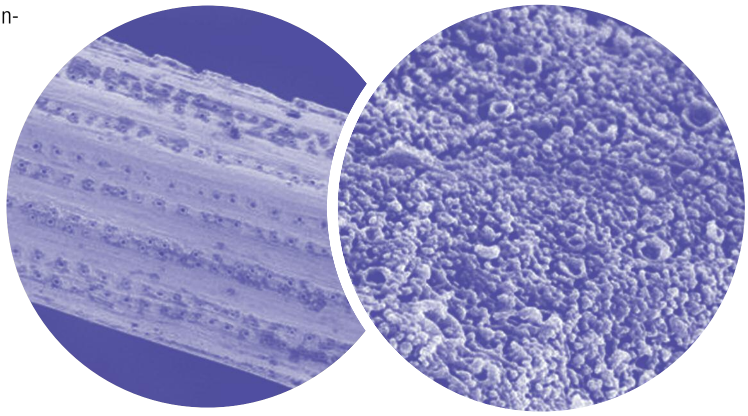
In spite of the fact that nanoscience is a rather mature discipline, it is astonishing that the width of easily accessible nanostructures is still rather small, i.e. most experiments are done with a very restricted set of chemical systems, such as Au or CdS. Many materials which are relevant for novel energy cycles and to catalyze more efficient chemical reactions simply do not exist as appropriate nanostructures, or their synthesis is highly non-sustainable and non-practical. Because of that, "de novo" nanosystems and nanosyntheses have to be designed from scratch. Some cases of the project portfolio are:

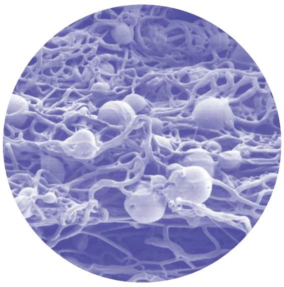
- Metal carbide and nitride particles offer new pathways for metal/base catalysis, but also are record holders in mechanical hardness or magnetization *(Dr. Cristina Giordano)*.

- This is also true for the corresponding metal borides and boronnitrides, which are new land for chemistry, when rational nanostructures are to be made *(Dr. Cristina Giordano)*.

- New cathode nanomaterials for the lithium batteries are another target where progress will directly impact society. Here, doping, superstructure formation and conductive coatings are additional issues to be addressed within synthetic protocols *(Dr. Maria Magdalena Titirici)*.

Synthesis development in these groups is always accompanied with the suitable physical characterization techniques. This includes, among others, high-resolution TEM microscopy, scattering techniques and magnetic characterization.





Artifical Photosynthesis

This international joint laboratory was established in July 2008 between the Max-Planck Institute of Colloids and Interfaces and Fuzhou University. 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.

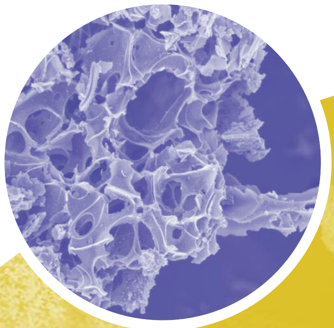
There are countless trials to establish stable systems for this purpose, mostly based on inorganic semiconductors with appropriately engineered band-gap and noble metals to promote the "extraction" of electrons. These materials include metal oxides, (oxy)sulfides, and (oxy)nitrides.

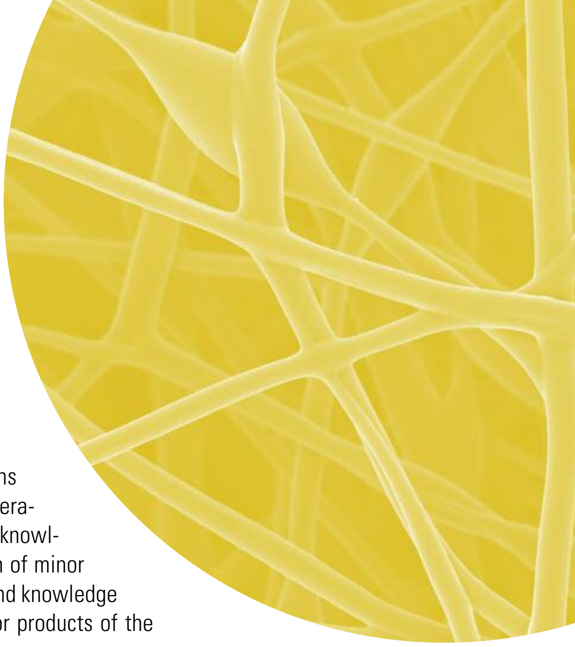
Our group investigates a new class of polymeric and organic-inorganic hybrid materials with controlled nanostructures as potential energy transducers for artificial photosynthesis. Potential applications include solar energy conversion, environmental purification, and a set of new reactions for organic synthesis. *(Dr. Xinchen Wang)*

Visions and Future Perspectives for the Next Years

The group is continuing its way from a phase of being diversified in many junior projects to a period with more coordinated research and longer term goals. As the TU Berlin has established a National Excellence Centre on Catalysis, it is a clear intention to further improve the cooperation with those colleagues. The gained scientific results from this cooperation are indeed more than only promising.

The previously started projects on "Energy Materials" and "Processes for the Raw Material Change" turned out to be very timely and secured the department in the last six years clear visibility and a leading European role in these activities. It is my personal intention to expand these activities. Partly driven by the colloid department, but also by the other departments, we progress with the internation





alization of our relations. Beside the well established Partner group at USCT/Hefei, we started a virtual "Artifical Photosynthesis Center" with the Fuzhou University, and establish an Exchange Program with Kyushu University. With the Thailand Nanocenter (NSDEC), we plan a massive program on "Nanoscience for Agriculture"

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,
- chromatographic lab including a number of modern chromatography techniques,
- reaction calorimetry with online multidetection,
- analytical and preparative ultracentrifugation,
- thermal analysis, DSC and porosimetry,
- GC- and LC-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. In science policy, I regularly act as a referee in DFG, European and International science evaluations. I am a board member of the ERACHEM defining the future tasks of chemistry on the European level. 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. In 2009, I received the Gold Medal of the UK Polymer group, which is a distinction for lifetime achievements, in 2011 I will receive the Binational Price for promoting French-German Scientific Cooperation.

Markus Antonietti,
Director of the Department
of Colloid Chemistry

HETEROPHASE POLYMERIZATION

Polymer Dispersions/Heterophase Polymerizations

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

Latex Crystals [1]

Monodisperse latexes form in gravitational fields highly ordered regions of fcc-lattice type. If the spacing of the lattice planes (d_{hkl}) is in the proper range, angle-dependent color effects are observed (**Fig. 1**).

Bragg reflection is detected perpendicular to the lattice planes for first order reflections if the condition $d_{hkl} \approx \lambda_0/(2\cdot n_D)$ is met. d_{hkl} is the lattice spacing, λ_0 the wave length of the Bragg peak, and n_D the refractive index. The surface distance between the particles is given by $d_{PP} = d_P \cdot \sqrt[3]{0{,}74/\ \Phi_P} - d_P$ and the center to center distance is $D = \sqrt{3/2} \cdot d_{hkl} = d_{PP} + d_P$.

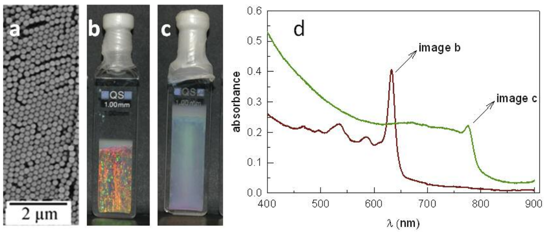


Fig. 1: SEM image (a), snapshots of a crystallized latex at high (b) and low (c) ionic strength, and their absorption spectra (d); d_p=229 nm

UV-Vis spectroscopy allows the determination of d_{hkl} and if the particle size and packing order are known, d_{PP} is accessible. A modified DLVO theory, with the assumption of a non-isotropic distribution of the ionic strength in the continuous phase, can be used to study the ordering of latex particles. It leads to an energy barrier counteracting the gravitational force and keeping the particles at distances which are in good agreement with the d_{PP} values estimated from UV-Vis measurements (**Fig. 2**).

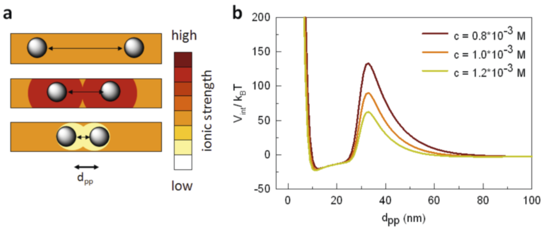


Fig. 2: Schematic illustration of non-isotropic ionic strength (a) and calculation results showing the appearance of an energy barrier counteracting gravity for varying concentration of 1:1 electrolyte (b)

Latex Particles with Special Morphology [2, 3]

Typically latex particles are of spherical shape surrounded by a hairy layer of less than 10 nm thickness. The origin of this layer is the hydrophilicity of the stabilizing groups which are attracted by the aqueous phase pulling neighboring carbon atoms away from the hydrophobic core. The greater is the chain length of the stabilizing polymers the lower their surface concentration. The morphology of such polystyrene particles (PS) stabilized by poly(ethylene glycol) (PEG) with a molecular weight of one million g/mol is very special (**Fig. 3, 4**). These particles are composed of triblock copolymers synthesized by ordinary radical heterophase polymerization. The radicals are generated via redox-reaction with ceric ions at the PEG chain ends that initiate polymerization of N-isopropylacrylamide (NIPAM). These diblock copolymers precipitate at the polymerization temperature of 60°C thus generating the reaction sites for the subsequently added hydrophobic monomers.

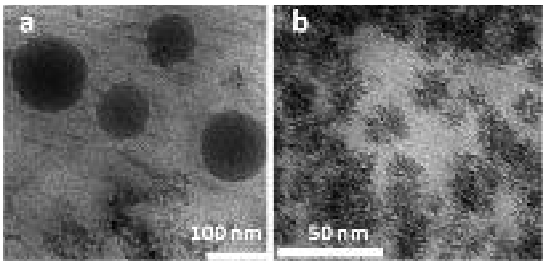


Fig. 3: TEM images showing the precipitation structure of PEG with an average molecular weight of one million (a) and diblock copolymer of PEG-PNIPAM as obtained after the first stage of the polymerization (b)

The morphology of the diblock PEG-PNIPAM precipitation structures looks bicontinuous as darker and brighter regions alternate and their size is quite monodisperse. The PEG-PNIPAM-PS triblock copolymer particles are of spherical shape and both the SEM and TEM images reveal a peculiar surface morphology (**Fig. 4**).

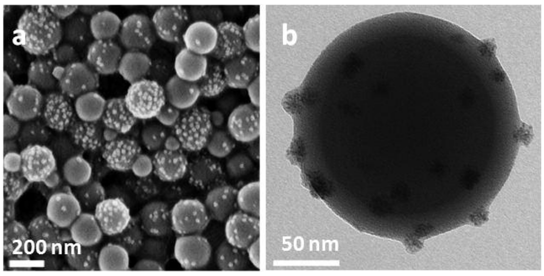


Fig. 4: SEM (a) and TEM (b) image of PEG-PNIPAM-PS triblock copolymer particles

The surface of the particles looks like sprinkled with buds of uniform size between 18 and 20 nm, but the number of (visible) buds per particle differs greatly. The size and shape of the sprinkles is alike the precipitation structure of the PEG-PNIPAM diblock precursor copolymer (image b of **Fig. 3**).

Distimuli-Responsive Block Copolymers [3, 4]

Block copolymers made of PNIPAM and poly(1 - (2 – acryloyloxyundecyl) – 3 –methylimidazolium bromide) which is an

References:

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ionic liquid polymer (PIL) are di-stimuli-responsive i.e. the PNIPAM block reacts on temperature changes and the PIL block on the concentration and nature of the counterions (**Fig. 5**).

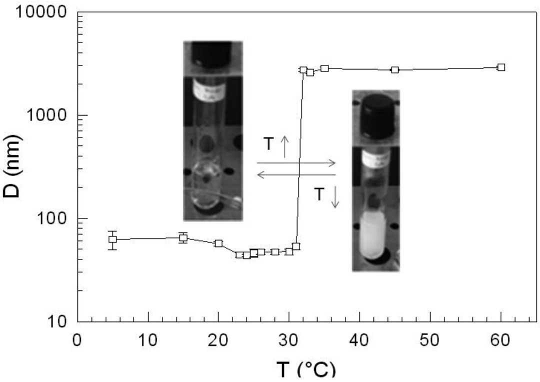

Fig. 5: Particle size (D) evolution of PIL-PNIPAM block copolymer in dependence on temperature showing the transition from solution to suspension at 60°C due to precipitation of the PNIPAM block

The PNIPAM block is hydrophilic below and hydrophobic above 60°C. Above this temperature macrophase separation leads to particles having PNIPAM cores and stabilizing PIL corona.

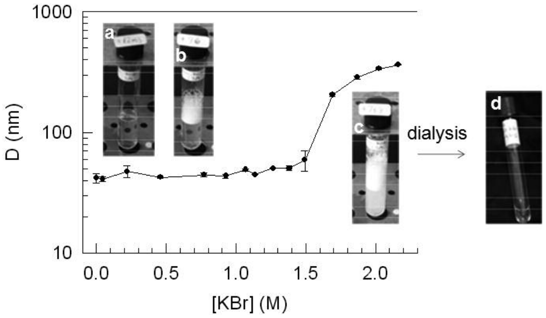

Fig. 6: Particle size (D) evaluation of PIL-PNIPAM block copolymer in dependence on KBr concentration showing the transition from solution to suspension, image (d) shows that the process is reversible if the excess KBr is removed by dialysis

The anion sensitivity of the PIL block is proven by the addition of KBr (**Fig. 6**). The diblock condenses above a certain Br^- concentration. In this system, while the PIL block is condensed, the colloidal stability appears provided by a corona of PNIPAM. Both transitions are fully reversible and can be repeated several times.

Composite Microcapsules [5, 6]

The combination of interfacial polycondensation and radical heterophase polymerization in an one pot multi-step reaction is an efficient way to produce composite microcapsules (**Fig. 7**). The first step is the emulsification of the template oil phase (pure styrene monomer or in combination with cyclohexane – chloroform 4:1 mixture), that contains terephthaloylchloride, and the oil-soluble radical initiator in an aqueous poly(vinyl alcohol) solution. In the second step, the polyamide capsule formation is started by the addition of an aqueous diamine solution at room temperature. Then, after one hour, the radical polymerization as third step is initiated by raising the temperature to 60°C.

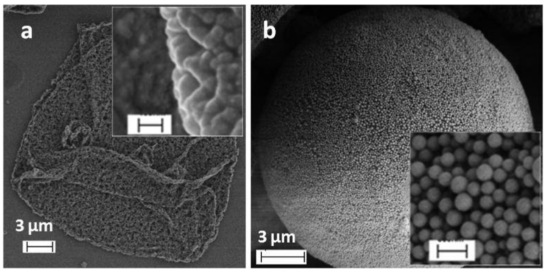

Fig. 7: SEM images of a polyamide (PA) capsule after polycondensation (a) and composite capsule after styrene polymerization (b) initiated with azobisisobutyronitrile; the bar of the insert in (a) and (b) represent 100 and 300 nm, respectively

The radical polymerization is not restricted to the PA capsules' interior but an ordinary emulsion polymerization takes place in parallel (**Fig. 7 and 8**).

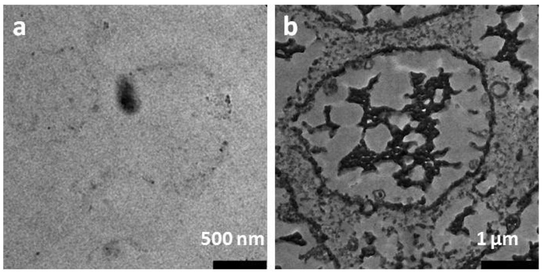

Fig. 8: TEM images of thin cross-sections of embedded PA (a) and composite capsule (b)

The morphology of the composite capsules depends strongly on the amount of styrene monomer in the oil mixture and the nature of the initiator.

K. Tauer, H. Essawy, H. Hernandez, O. Kiryutina, K. Krüger, J. Texter, N. Weber, U. Lubahn, S. Pirok, I. Shekova
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From Polymer Synthesis to Porosity Analysis

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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 Laboratory, Stockholm University, Sweden)
Since 2009: Group Leader – Porous Polymers (MPI of Colloids and Interfaces, Potsdam)

High-Performance Polymers such as aromatic poly(imide)s or poly(benzimidazole)s are an important class of polymers in a variety of applications that are related to energy technologies (e.g. gas separation, fuel cell membranes etc.)**[1]**

These applications can often benefit from the presence of a well-defined meso- or microporosity. Although a lot of progress has been achieved in the synthesis of porous polymers during the last years, there is still a lack of understanding with regard to the stability of such small pores (< 10 nm) in "soft" polymeric materials. Furthermore, the synthetic pathways towards porous high-performance polymers are still limited to classical petrochemical routes, which should be overcome to achieve truly sustainable polymer chemistry.

New Synthetic Pathways

The classic synthesis of aromatic high-performance polymers requires typically the use of high-temperatures and harmful organic solvents such as m-cresol etc. Recently, there was an increased interest in the ionothermal synthesis of polymers and polymer networks. The use of inorganic salt melts (e.g. LiCl/KCl) can be beneficial for the synthesis of polybenzimidazole (PBI), a polymer which requires typically harsh synthetic conditions (use of strong acidic solvents or toxic byproducts such as phenol) **[2]**. Besides molten salts, we are also interested in the use of molten salt hydrates or just plain hot water (hydrothermal synthesis) as effective solvents for polymer synthesis.

Furthermore, we are interested in the use of natural resources (e.g. lignin or birch bark extracts) as monomer resources.

Mesoporous Polymers

Mesoporous polymers, i.e. polymers having pore sizes between 2 and 50 nm, are far less investigated compared to their inorganic counterparts such as mesoporous silica or metal oxides. This is somewhat surprising regarding the high potential of mesoporous materials in a number of applications (e.g. separation science, controlled release, etc.).

We have an interest in both, the synthesis and characterisation of mesoporous polymers. There is still a need to develop new synthetic routines towards mesoporous polymers. Furthermore, the stability of mesopores against collapse as well as the details of pore collapse are widely unexplored. We use gas sorption together with scattering techniques and thermoporometry to analyse mesoporous polymers.

From a synthetic point of view, we focus mainly on the hard-templating pathway, which involves the replication of silica nanostructures, such as nanoparticles.

Recently, this pathway was used for the synthesis of mesoporous polystyrene and polyacrylate gels. **[3, 4]** The cross-linking density of the gels was varied between fully and non cross-linked, which allows a more detailed analysis of the mesopore stability against solvent and temperature treatments.

Fig 1 shows exemplary FESEM micrographs of mesoporous polystyrene (PS) which was subjected to various temperatures. It is obvious that pore collapse sets in already at temperatures well below the nominal glass transition of PS. This is due to the nanosized pore walls which are affected by a lowering of T_g.

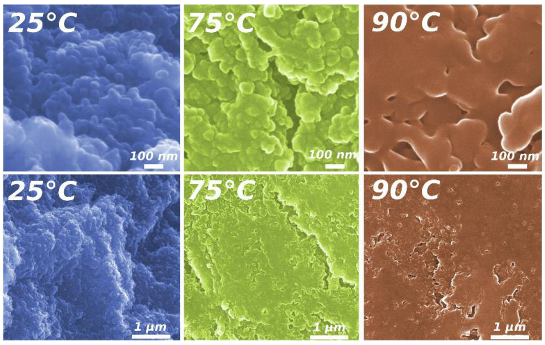

Fig. 1: FESEM images of mesoporous PS subjected to varying temperature. Pore collapse sets in already at 75°C, which is ~25°C below the glass transition temperature of PS

The analysis of the freezing/melting behaviour of solvent which is confined within mesopores can also be used to analyze mesoporous systems (thermoporometry). The phase transition temperatures are lowered due to the presence of highly curved interfaces. This techniques allows the analysis of solvent-swollen systems, such as mesoporous hydrogels (**Fig. 2**). By comparison with dry samples, it could be shown that the pore collapse can be reversible. That is, at low cross-linking degree no porosity is observed in the dry state, but the pores open up again upon solvent treatment. The results of SAXS analysis were consistent with the thermoporometry results.

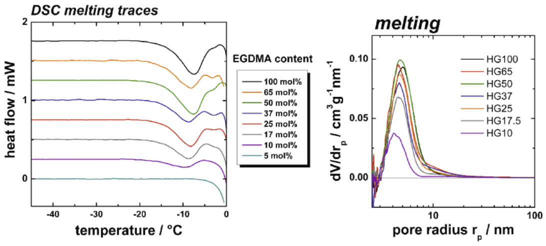

Fig. 2: DSC melting traces (left-hand side) of water confined within mesoporous hydrogels with varying cross-linker degree and the respective pore size distributions (right-hand side)

Microporous Polymers

Microporous Polymers are of high interest, both from an academic and commercial point of view. They could find applications in gas separation/storage, sensor or optoelectronic applications.

The analysis of soft microporous matter was however not developed at the same pace as the synthesis. This might be due to the main problems associated with the analysis of soft, amorphous matter: swelling and deformation effects.

We are interested in the synthesis and characterization of both: cross-linked and non cross-linked microporous polymers. Characterization is mainly performed on the basis of gas sorption, using various probes (nitrogen, argon, carbon dioxide and hydrogen). The results are cross-checked by additional methods like X-ray scattering and NMR-techniques.

In this way it is possible to overcome problems associated with the use of nitrogen sorption alone, such as slow kinetics, liquid plugs etc.

As an example, we analyzed intrinsically microporous polyimides in dependence of their molecular geometry and the processing (precipitation vs. solution casting). **[5, 6]** Carbon dioxide and hydrogen can reliably probe much smaller pores than nitrogen. Hence, it was possible to determine the limits of intrinsic microporosity with regard to molecular properties (chain geometry and flexibility) in more detail. Only polymers that are not capable of adsorbing H_2 and CO_2, can be regardded as truly non-porous (non-connected and non-accessible free volume). Additionally, the influence of processing can be analyzed (**Fig. 3**). By that, significant differences of the applied methods (such as different analysis temperatures) became obvious. These effects need more clarification within the next years.

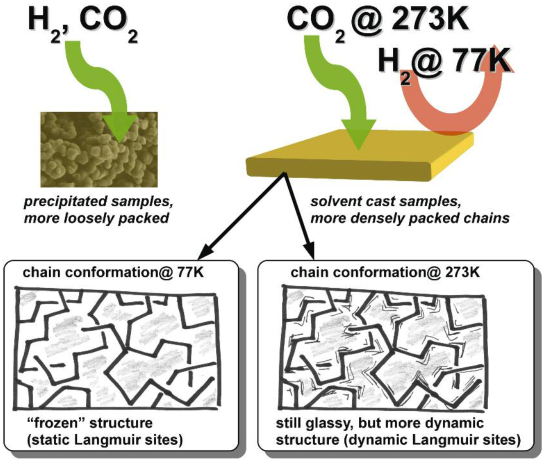

Fig. 3: Overview on the observed differences in gas uptake of microporous polyimide upon different processing (upper part) and sketch of the underlying temperature dependent microstructure

Another example is a case study on microporous networks, which had the intention to identify reliable methods for the extraction of important parameters (specific surface area, pore size and volume) from gas sorption and ^{129}Xe-NMR data.**[7]** Swelling effects could be clearly identified and their impact on the determination of the pore size distribution was analyzed. A major result of these studies is the dynamic character of the micropores. It seems quite likely that they can adopt their pore size by elastic deformations to their environment (dry atmosphere, solvent filled, etc.). This has severe implications on the application of such materials.

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Bioinspired Polymers and Colloids

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Biohybrid copolymers are interesting materials for the bioinspired generation of "smart" functional colloids and hierarchical structures, for usage in for instance life science applications. Advanced new materials (polypeptides, pseudopeptides, glycopolymers, etc.) are prepared by controlled polymer synthesis techniques and studied according to their complex or higher-order self-assembly in solution or in solid state.

Synthesis

Radical thiol-ene ("click") photochemistry has been applied to the modification of well-defined copolymers based on polybutadienes **[2]**, polyoxazolines **[1, 4]**, and polypeptides **[13]**. In addition, the concept has been extended to the heterophase functionalization of polymer colloids **[7]** and inorganic surfaces, i.e. glass fibers and slides (**Fig. 1**) **[8, 10]**. Particular emphasis was put on the preparation of sugar-containing materials.

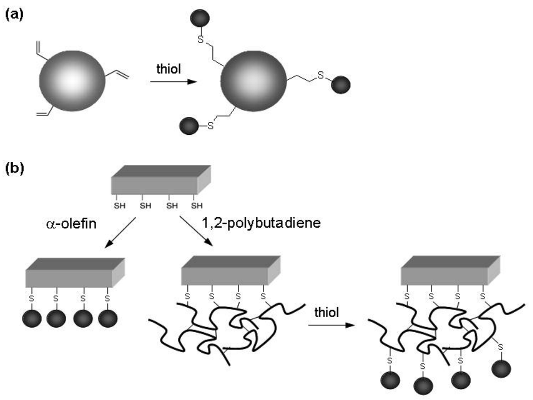

Fig. 1: Schematic illustration of the heterophase thiol-ene functionalization of (a) colloids and (b) surfaces.

Polymer Self-Assembly

Glucosylated polybutadiene-poly(ethylene oxide) (PB-PEO) block copolymers formed very large vesicles of greater than 500 nm in diameter by direct dissolution in water. The existence of unilamellar vesicles could be confirmed by light scattering analyses (DLS/SLS) and transmission electron microscopy (TEM). Chains can only be packed in a monolayer, accordingly these vesicles should have an asymmetric membrane with different hydrophilic layers on the outside and on the inside (**Fig. 2a**). 2D-NOESY-NMR experiments indicated that the glucose (Glc) units are spatially separated from the PEO chains (**Fig. 2b**), and surface-enhanced Raman spectroscopy provided evidence that glucose is located on the outside and PEO on the inside **[2]**.

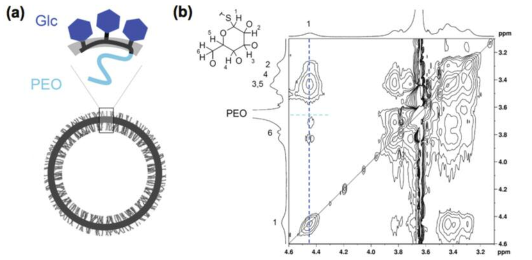

Fig. 2. (a) Schematic illustration of a glycopolymer vesicle with an asymmetric membrane and (b) 2D-NOSY-NMR spectrum (500 MHz) of glucosylated PB-PEO block copolymer vesicles in D_2O; the missing cross peak between Glc CH and PEO indicates spatial separation of the two hydrophilic moieties.

Poly[2-(4-(β-D-glucosylsulfanyl)-butyl)-2-oxazoline] in water formed nanotubes measuring several hundreds of nanometers in length, as observed by scanning force microscopy (SFM). The diameter of the tubes was found to be 4–9 nm, and the thickness of the wall was about 1 nm (small-angle X-ray scattering, SAXS). Formation of the tubes should occur via a 2D hydrogen-bonded layer of interdigitated polymer chains undergoing bending and closing to a tube. Supporting the idea of a hydrogen-bonded structure, the nanotubes were not observed in 8 M aqueous urea or in PBS buffer solution **[4]**.

Poly(2-isopropyl-2-oxazoline) (PIPOX) homopolymers can be crystallized in hot aqueous solution at a temperature above the cloud point temperature, producing uniform microparticles with internal fibrous structure (**Fig. 3**) and a melting point close to 200°C. It was proposed that hydrophobic and oriented dipolar interactions promote a slow crystallization of chains to form nanoribbons, which then fuse together to form nanofibers. These nanofibers assemble into microspheres, which, however, could be suppressed by the presence of small amounts of a co-solvent (e.g. ethanol or tetrahydrofuran) or surfactant (e.g. sodium dodecylsulfate) **[11, 16]**.

The kinetics of the crystallization process and time-dependent evolution of the morphology were studied using wide-angle X-ray scattering (WAXS) and cryogenic/conventional scanning electron microscopy (SEM). The results indicate that the temperature-induced phase separation of dilute aqueous PIPOX solutions produced a bicontinuous network-like structure (**Fig. 4a**). With the onset of crystallization after ~4 h (for 1 wt% PIPOX in water at 60 °C) the network collapses into individual particles composed of a porous fiber mesh. These "premature" particles then act within the next ~5 h as nucleation sites for secondary crystallization. Nanofibers preferentially form at the particle surface, thus wrapping the microspheres like a ball of wool (**Fig. 4b**). This stage is characterized by a steep increase in the crystallinity of the material. Crystallinity reaches a plateau after 8-10 h, when most of the amorphous material is depleted. At this time, compact and isolated microspheres of uniform size have been formed **[14, 16]**.

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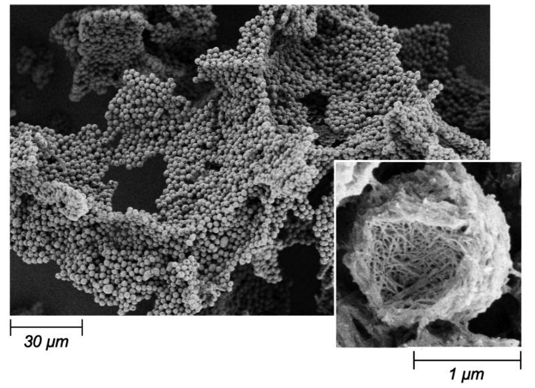

Fig. 3: Scanning electron micrographs of crystalline PIPOX microparticles with hierarchical structure.

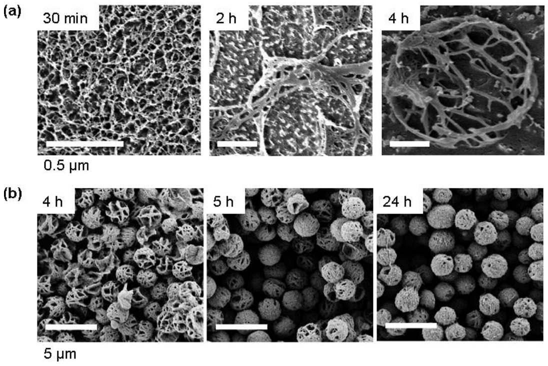

Fig. 4: Evolution of the morphology produced during the annealing of a 1 wt% aqueous solution of PIPOX as visualized by (a) cryogenic SEM (t ≤ 4 h) and (b) conventional SEM (t ≥ 4 h); the onset of crystallization occurred at t ~ 4 h (WAXS).

Biofunctional Colloids and Surfaces

Glycosylated microspheres were obtained by the crystallization of poly[2-(isopropyl/3-butenyl)-2-oxazoline] (5 mol-% of unsaturated units) from aqueous solution above its cloud point, followed by the covalent attachment of 1-thio-β-D-glucose or galactose using thiol-ene chemistry (60% conversion of double bonds). The carbohydrate moities on the surface selectively interacted with lectins and the microspheres could thus be employed as "fishing rod" for the isolation and separation of specific lectins, i.e. ConA and RCA I, from a mixture (**Fig. 5**) **[7]**.

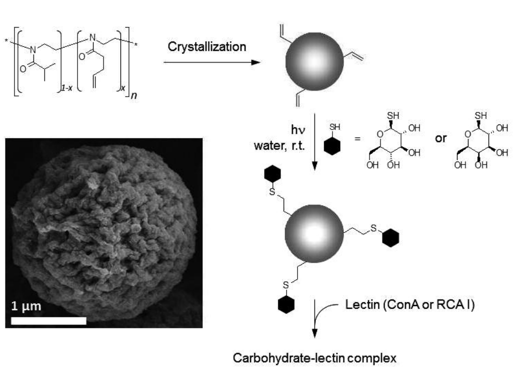

Fig. 5: Preparation of polyoxazoline-based crystalline microspheres for carbohydrate-protein (lectin) recognition; image shows the scanning electron micrograph of a freeze-dried glucosylated microsphere.

Sulfhydrylated glass slides were functionalized with 1-allyl-α-D-glucopyranoside and analyzed according to the ability to selectively bind to the lectin Con A **[8]**. For this purpose, glucose-coated glass slides were incubated with a solution of fluorescent Con A, and the interaction between the sugar units and the lectin were monitored by fluorescence microscopy. The degree of lectin binding was rather low, but could be considerably increased upon inclusion of a flexible polymer layer (**Fig. 1b**).

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MODERN TECHNIQUES OF COLLOID ANALYSIS

Electron Microscopic Studies of Colloidal Systems and Biomaterials

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The study of structure/property, structure/function and chemical synthesis/structure relationships of both natural and synthetic colloidal and biological materials is one of the main topics of the research at the MPI of Colloids and Interfaces. Hierarchical structured biological and biomimetic materials and hybrid materials, active coatings and interfaces, functional supramolecular organizates, the synthesis of bio-inspired polymers, novel synthetic inorganic nanoparticles and organic-inorganic hybrid materials, porous polymers, functional carbonaceous materials and the synthesis polymer particles are in focus on the interdisciplinary research in the institute. Transmission, high-resolution scanning and environmental electron microscopes are powerful tools to investigate the morphological ultra-structure with a high electron optic resolution. The electron microscopy lab is a so called service lab to perform scientific routine measurements for the whole institute. Some selected interesting results are presented here.

Controlled nanoparticle aggregation is a topic of our scientific interest. The nanoparticle aggregation based growth of calcite crystals, which can be tuned by regulating the concentrations of calcium ions and the polyelectrolyte additive in aqueous solutions. Using the random copolymer polyelectrolyte poly(4-styrene sulfonate)-*co*-(maleic acid) (PSS-*co*-MA) considerably guides crystallization of calcium carbonate (CC) with a high versatility. The bio-inspired non-classical crystallization protocol yielded a series of calcite microstructures. Simple variation of calcium and polyeletrolyte concentrations enables a systematic control over the size and morphology of particles among pseudo dodecahedra, pseudo octahedra, multilayered spheres and hollow spheres **[1]**. In order to gain more insight into the formation of calcite pseudo dodecahedral single crystals, the particles obtained at a much lower PSS-*co*-MA concentration (2.5 mg/L) but the same CaCl$_2$ concentration (1.25 mM) was characterized by high-resolution scanning electron microscopy (HRSEM). As shown in **Fig. 1**, the intermediates obtained after 1 week are microparticles with different shapes. We also attempted to evoke shape control by face selective polymer adsorption after introducing foreign seeds at the start. The seed for the shape conversion process was chosen to be rhombohedral calcite particles. When PSS-*co*-MA of 0.1 g/L was used as the aqueous solution medium for the morphogenesis, only slight truncation at edge sites was observed. Using a mixture of PSS-*co*-MA and CaCl$_2$ of 1.25 mM, the resultant crystals became larger in size with time indicating particle growth (Fig. 1c) and displayed sleek edges after 2 weeks.

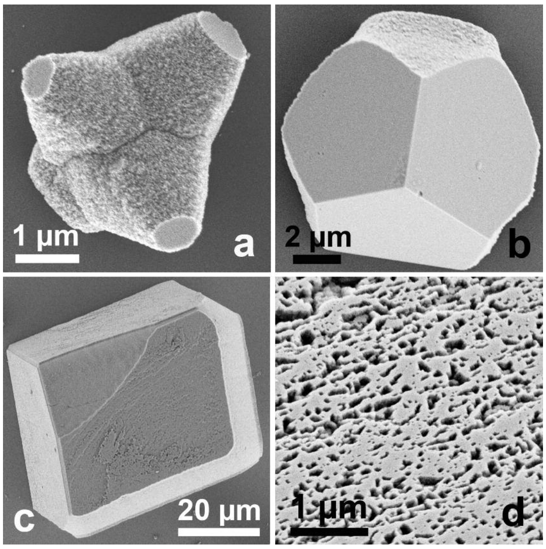

Fig. 1: Calcite particles with curved rhombohedral surface shape (a) and pseudo dodecahedral shape (b), rhombohedral calcite particle (c) with etching pits on {104} faces (d)

These edges were formed by face selective polymer adsorption while the {104} faces also show etching pits (**Fig. 1d**) through irreversible dissolution. Rhombohedral calcite single crystal seeds in a growth solution containing the polymer do not produce pseudo dodecahedral morphology but a rhombohedron with truncated edges due to face selective polymer adsorption in a classical growth process.

One interesting subject is the crystallization of polymers from solution induced by liquid-liquid phase separation. In order to clarify the crystallization mechanism and to elucidate the evolution of the formed spherical morphology, the crystallization of the thermo-responsive poly(2-isopropyl-2-oxazoline) (PiPOx) in aqueous solutions by systematic variation of temperature and polymer concentration **[2]**. Upon heating e.g. a clear 1 wt.-% aqueous PiPOx solution above the cloud point phase separation takes place. After annealing the system at 60°C freeze-dried samples were investigated by HRSEM. The droplet-like particle morphology obtained after 3 h (**Fig. 2a**) at 60°C showed closed surface structure. However, after 4 h annealing, the morphology considerably changed (**Fig. 2b**). The spherical and rather porous particles have a diameter of around 2 µm, whose framework shows a fibrillar structure. Besides, bending layers of fibers and hollow hemispheres are observed. These premature particles did not grow in size but the cavities became smaller until compact, isolated particles of regular size and shape was obtained (**Fig. 2c,d**). However, the general morphology was maintained at longer times of annealing and the structure appeared to be stable over time. This might be used to tune the properties of the crystalline microspheres for various applications, e.g. in chromatography.

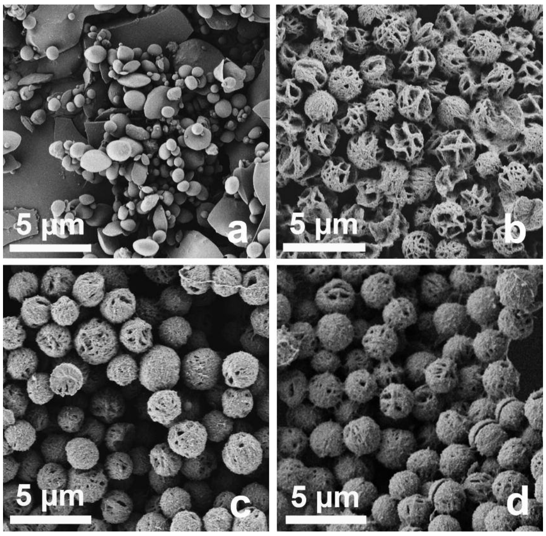

Fig. 2: PiPOx Particles grown for 3 h (a), 4 h (b), 24 h (c) and 120 h (d).

Another interesting project is the electron microscopic characterization of microporous and mesoporous carbon materials formed by template-free preparation of dicyanobiphenyl (DCBP). The influence of the experimental conditions (salt/monomer ratio, temperature, heating rate) for the DCBP monomer to understand and adjust mesopore formation was studied **[3]**.

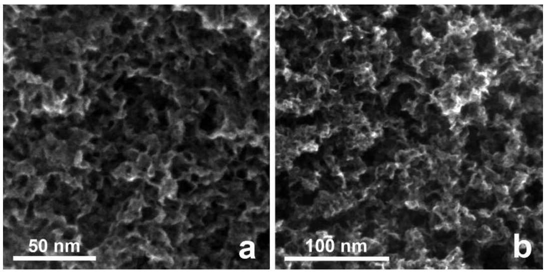

Fig. 3: Mesoporous structures prepared from DCBP with 5 (a) and 10 (b) equivalents of $ZnCl_2$

The ionothermal polymerization of DCBP in an excess of $ZnCl_2$ at 400°C produces an amorphous material with high surface area and micropores of the order of 2 nm in size. Mesopores are formed at a higher reaction temperature (600°C) in addition to micropores. The shape of the nitrogen adsorption-desorption isotherms completely changes from 2 to 20 equivalents of salt, reflecting an extreme increase of the size of the mesopores. A formation of larger pores is presumably due to the onset of phase separation between the forming carbonaceous polymer and the salt phase. As phase separation should have an influence on the morphological structure, HRSEM investigations were carried out (**Fig. 3**).

The prepared materials are highly homogeneous and macroscopic heterogeneities are absent on all scales. Samples prepared from DCBP at 600°C with 5 equivalents of $ZnCl_2$ constist of mesopores with sizes of up to 5 nm and an interconnected, droplet-like porosity (**Fig. 3a**). Bigger pores (>10 nm) of the material are formed by using 10 equivalents of $ZnCl_2$ (**Fig. 3b**). Such morphologies are similar to those of gels obtained from spinodal demixing and favorable for transport and permeation.

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Sustainable Functional Nanostructured Materials

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The concept of Sustainable Chemistry represents an area of innovation, which not only preserves resources, but also stands for a development process in the chemical industry. Sustainable Chemistry aspirates to raise the stake of less dangerous chemicals as well as production of environmentally high-quality products from preferable renewable resources.

Our research is focused on the production of nanostructured materials of practical importance starting from low cost natural precursors and using environmentally friendly processes. It is known that a material, regardless if organic or inorganic improves its properties when scaled down to the nanometer region. Therefore mesoporous nanostructured materials such as polymers, carbons or metal oxides produced via a green chemistry route can offer attractive fields of applications e.g. in catalysis, chromatography, adsorption, sensors, energy storage and electrochemical processes.

a) Nanostructured Carbon Materials

Carbons (glassy carbons, activated carbons, coals, porous graphitic carbons) have been used by mankind since many years and they touch every aspect of our daily lives. The synthesis of carbonaceous materials generally relies on very harsh conditions e.g. electric-arc discharge techniques, catalytical chemical vapour deposition, catalytic pyrolysis of organic compounds or high-temperature hydrothermal conversion at 800°C from amorphous carbon.

Therefore, the search for new strategies to generate carbon materials, carbon hybrids and related materials has been of major importance in material chemistry. Hydrothermal carbonization, involving the hydrothermal decomposition of various carbohydrates in aqueous solutions at 180°C, represents one of these strategies, being a green and cheap method to directly produce spherically shaped functional carbon from carbohydrates (**Fig. 1**) **[1, 2]**. The reaction mechanism for the formation of the carbon spheres involves the dehydration of the carbohydrate in the first step and subsequent polymerization and carbonization of the so-formed organic compounds in the second step **[3]**. A major advantage of this method is that due to the mild temperature conditions the as synthesized particles contain functional groups confined to the surface and thus are hydrophilic. Therefore further activation processes are not necessary. Additionally, this enables us to further functionalize the particles in order to fit various applications.

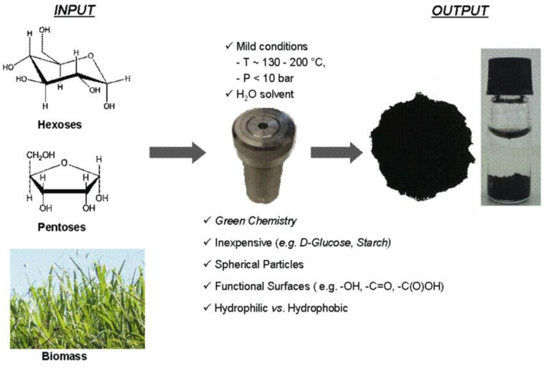

Fig.1: Hydrothermal carbonization process

The porosity of hydrothermal carbon can be controlled by introducing suitable templates into the synthesis **[4, 5]**. Thus, performing the hydrothermal carbonization in the presence of various nanostructured silica or alumina (as hard templates) or block copolymers or latexes (as soft templating) **[6, 7]** followed by removal of templates, mesoporous functional hydrophilic carbons materials are easily obtainable (**Fig. 2**). Such a low temperature route towards porous carbon materials with controllable surface functional groups and reactivity has a great potential for a variety of applications such as catalysis, chromatography, adsorption and Li insertion.

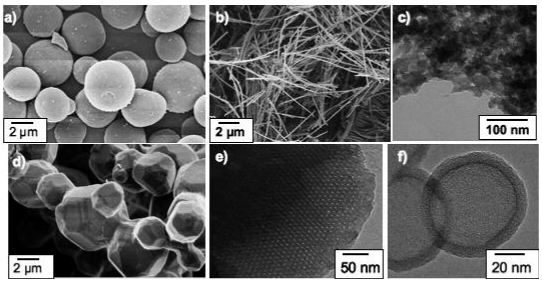

Fig.2: Nanostructured hydrothermal carbonaceous materials:
a) mesporous carbon spheres obtained via HTC in the presence of nanostructured silica templates; b) tubular carbon obtaining via HTC in the presence of macroporous alumina membrane; c) carbon aerogel from glucose in the presence of borax; d) e) mesoporous carbon obtained via HTC of fructose in the presence of pluronic F127 block copolymer f) hollow carbon spheres obtained using HTC of glucose in the presence of latex nanoparticles

Another very interesting aspect of the hydrothermal carbonization process is that instead of pure carbohydrates, low value biomass residues can be used as a carbon precursor. We are currently investigating the mechanism of the HTC process of rye straw in comparison with pure carbohydrates and the important factors which influence it **[8]**. Biomass conversion is a meaningful way to transfer biomass into useful materials, more efficient energy carriers and/or carbon storage deposits. Transfer of biomass towards carbon rich, coal-

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like derivatives is one option to sequester carbon and the stored energy from plant material. This represents also an efficient process to remove atmospheric CO_2 by fast growing plants; finally forming a carbon sequestering solid witch can be then mixed with soil with various effects on the plant growth **[9, 10]**.

b) Carbon Nanocomposites

Carbon nanocomposites display versatile allotropic morphologies, physical-chemical properties and a wide range of applications such as mechanical, electronics, structural material, chemical processing and energy management. Using hydrothermal carbonization in the presence of water soluble metal salts, or preformed nanoparticles we can obtain carbon/metal (oxide) nanocomposites in one step process **[11]**. These nanocomposites have important applications in the field of catalysis and electrochemistry. For example the hydrophilic C/Pd carbon nanocomposites were successfully used for the selective hydrogenation of phenol to cyclohexanone in aqueous phase **[12]**, while Pt on carbon aerogels as successful catalysts for methane direct oxidation to methanol **[13]**. Furthermore, the carbon matrix can be removed from these nanocomposites by simple calcination. Incorporation of a titanium containing precursor into the HTC process produces a nanostructured C/TiO_2 composite with visible light photocatalytic properties. **[14]** Additionally $LiFePO_4$/C mesocrystals with hierarchical porosities with (**Fig. 3**) can be produced in one step reaction for successful used as cathode in Li Ion Batteries **[15]**.

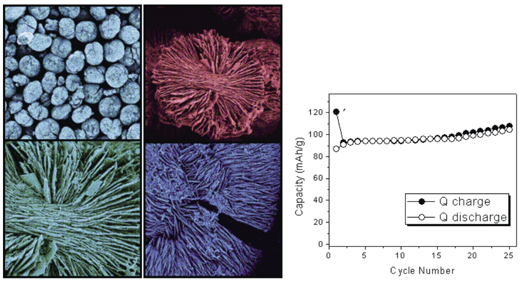

Fig.3: left: SEM micrographs of the $LiFePO_4$/C mesocrystals at various magnifications; right: charge/discharge capacity vs. cycle number plot for the $LiFePO_4$/C mesocrystals

c) Nitrogen Doped Carbon

The properties of carbon materials are dependent, to a large extent on the raw material, surface structure and porosity. However, the greatest effect on physicochemical properties of activated carbons is exerted by heteroatoms that are built into their structure (oxygen, nitrogen, boron, halogens, etc)

Recently, nitrogen-containing carbons are the subject of particular interest to researchers due to their remarkable performance in applications such as CO_2 sequestration, removals of contaminants from gas and liquid phases, environmental protection industry, catalysts and catalysts supports, or in electrochemistry as supercapacitors, cells and batteries to improve their capacity parameters.

The methods for the production of such materials relay normally on very harsh and multistep processes, which involve high temperature production of carbon materials followed by introduction of nitrogen to the structure using ammonia, amines or urea.

Here we present green and sustainable alternatives to produce nitrogen rich carbons which are based on the hydrothermal carbonization of nitrogen containing carbohydrates such as chitosane or glucosamine **[16]** or on hydrothermal carbonization of glucose in the presence of proteins **[17]**. The later approach leads to the production of carbon aerogels with high porosities, containing up to 9% nitrogen in their structures even at high post treated temperatures. This process and some SEM/TEM micrographs of such materials are shown in **Fig. 4**.

Another approach towards N doped porous carbons is simply taking see food waste products which contain high amounts of chitin as well as $CaCO_3$, followed by carbonization and removal of the inorganic using acetic acid. Thus the $CaCO_3$ can be used as a sacrificial template to obtain a high surface area material while the chitin is a suitable precursor for the production of N doped materials **[18]**.

Given the simplicity of this method and the low cost of the starting precursors we believe that this method represents a sustainable alternative for the production of nitrogen containing materials. Such materials have been applied already in important applications such as for example supercapacitors. Thus, the materials produced from glucosamine, followed by chemical activation turned out to be very promising candidates for electrodes in superacapacitors. This is due to the fact that besides the high surface area, they also contain up to 8 %N within their structure which leads to an increase in capacity (~ 300 F/g) related to some redox reaction with the electrolyte **[19]**. Furthermore the same N-doped materials also proved to have a significant uptake and selectivity for CO_2 versus N_2 **[20]** as well as a very high thermal and electrical conductivity **[21]**.

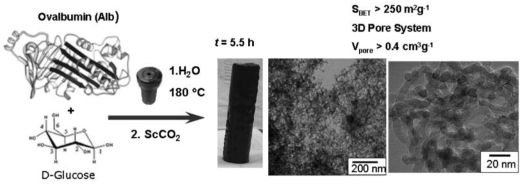

Fig. 4: Schematic process illustrating the production of nitrogen doped carbon aerogels from albumine and glucose together with two TEM micrographs illustrating their highly porous structure

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De Novo Nanoparticles:
Novel Synthetic Routes for Nanoparticle Production

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1. Introduction

In 1857, Sir Michael Faraday prepared a sample of pure colloidal gold and described it for the first time in scientific terms. Faraday's work was inspired by the alchemist Paracelsus **[1]** and has driven generations of scientist toward nanomaterials. The remarkable properties exhibited by nanoscale materials are nowadays well-known and investigated mostly for metals and metal oxides, but just partially studied for other materials, such as metal nitrides (MN) and metal carbides (MC).

MN/MC nanostructures show potential in a diverse range of applications due to their unique properties. The most important placing them at the borderline between metals and ceramics, being e.g. conductive and active catalysts as pure metals but, at the same time, harder, longer lasting and resistant in harsh conditions. All these characteristics make them a valid and/or complementing alternative to pure elements or metal oxides.

Motivated by these appealing features, we set up a general, safe and competitive synthetic procedure to simplify and potentially scale up MN/MC production as nanostructures. Through complexation of metal complexes by urea molecules (or close derivatives), gels are formed which enable to use all shaping processes of classical sol-gel chemistry.

In this route, familiarly addressed as "the urea-glass-route" **[2]**, urea plays the double role of nitrogen/carbon source and stabilizing agent, and allows the production of a wide set of nanosized and highly crystalline metal carbides and nitrides with high specific surface area (up to 400 m^2/g) **[3]**.

As an example of their potentialities, as prepared iron carbide, molybdenum and tungsten carbides/nitrides nanoparticles have been tested as catalysts in ammonia decomposition process (a process for CO free hydrogen production, e.g. for fuel cell applications). The first promising results place these materials as a valid alternative to conventional catalysts (currently ruthenium based systems) **[4]**.

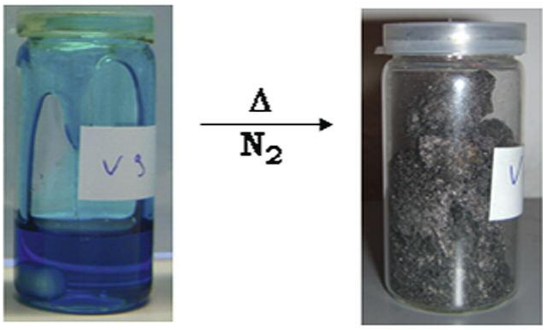

Fig.1: Vanadium-urea gel-like starting material (left side) and corresponding VN powder after heating treatment (right side).

2. Magnetic Nanostructures and Novel Ferrofluids

Seeking for alternative magnetic materials to iron oxide, we focused our attention to iron nitride and carbide, due to the higher stability against oxidation (compared to elemental iron), superior magnetic properties (compared to FeO_x) and an extreme hardness. In particular, Fe_3C can rank as an ideal candidate to extend Fe° and FeO_x in nanoapplications, say as an MRI contrasting agent or for the generation of stronger ferrofluids. Crystalline Fe_3C nanoparticles (d~ 7 nm) can be easily obtained by the soft urea pathway **[5]** and can be dispersed in water using a PEG based surfactant, generating a novel iron carbide based ferrofluid.

Simply by playing with external parameters such as iron precursors, C-source, use of hard template or additives, nanosized Fe_3C with different morphology (specifically nanoparticles and mesoporous material) have been obtained **[3, 4]**.

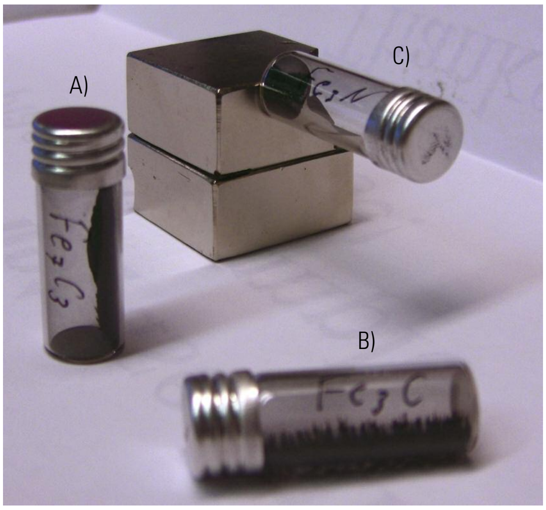

Fig. 2: Selection of as prepared magnetic materials: A) Fe_3C, B) Fe_7C_3 and C) Fe_3N.

3. Bio-Templating of Metal Carbides and Nitrides

In order to better control nucleation and growth of the intermediate ceramic phases, a biotemplating based route to metal carbides and nitrides has been developed. By dispersing aqueous metal salts within a biopolymer matrix, the nucleation of these intermediate precursors (often an oxide phase) is constrained to the nanoscale. On further heating, the carbon or nitrogen-rich decomposition products of the biopolymer react with these oxide nanoparticles, forming carbide **[6]**, or nitride nanoparticles.

Substituting single biomolecules with hierarchical biological template, we found out that the complex microstructure can be fully template. In particular, the complex structure of leaf veins with the magnetic material Fe_3C has been shaped. **[7]**

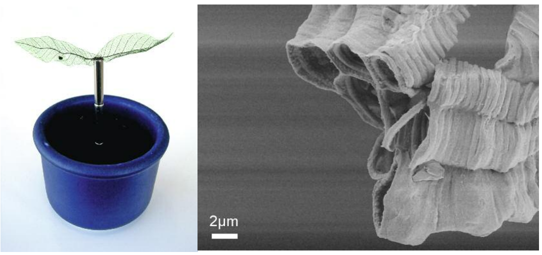

Fig. 3: Metaphoric picture (A) and SEM image (B) of the magnetic sacred fig (ficus religiosa) leaf replica, showing helical pitted structure characteristic of the replicated xylem vessels.

4. Advanced Nanofibres

Particulates are surely the simplest and easiest systems to handle in nanoscience, however non-spherical morphologies including anisotropic shapes such as nanofibres can bring additional features (e.g. anisotropic magnetism and optical properties). Electrospinning is a well-developed technique for fiber generation, from micro to nanometers. By combining the urea glass route **[2, 3]** with electrospinning techniques, it was possible to design various nanostructured fibers simply by structuration and calcination of the gel precursors. **[8]**

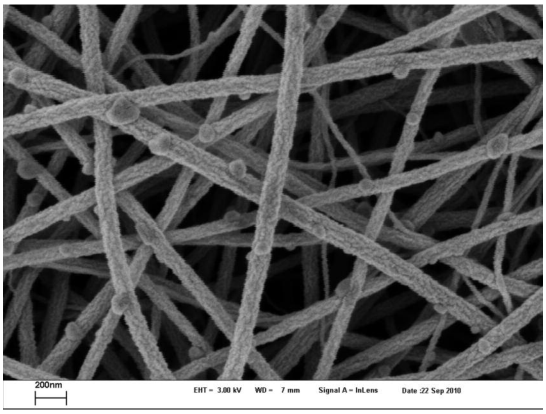

Fig.3: Fe_3N nanofibres prepared by polymer assisted urea glass route, at 600°C.

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Artificial Photosynthesis

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Natural photosynthesis feeds nearly all life on Earth either directly or indirectly by converting solar energy, carbon dioxide, and water into hydrocarbons and oxygen. It has inspired artificial versions of photosynthesis, i.e. the splitting of water into its constituent elements and the conversion of carbon dioxide into organics via sunlight. An important challenge in artificial photosynthesis is to develop efficient, stable, and inexpensive catalysts capable of harvesting visible light. There are countless trials to establish stable systems for this purpose, mostly based on inorganic semiconductors. We are investigating polymeric and organic-inorganic hybrid materials with controlled electronic, optical, and textural structures as potential energy transducers for artificial photosynthesis.

Synthesis of New g-C_3N_4 by Co-polymerization

We recently introduced graphitic carbon nitride (g-C_3N_4) as a metal-free photocatalyst **[1, 2]**. This offers new opportunities for solar energy applications, because covalent carbon nitrides are polymeric, cheap, abundant and stable materials with easily-controllable surface and bulk properties. Nevertheless, there are some drawbacks for this new photocatalyst, such as insufficient sunlight absorption ($\lambda<460$ nm) and low quantum efficiency. To solve these problems, a co-polymerization approach was developed to synthesize new carbon nitride structure, see **Fig. 1**. After co-polymerization with barbituric acid (BA), a remarkable red-shift of optical absorption from 470 to 750 nm and a 5 times higher activity of hydrogen production can be achieved. **[3]**

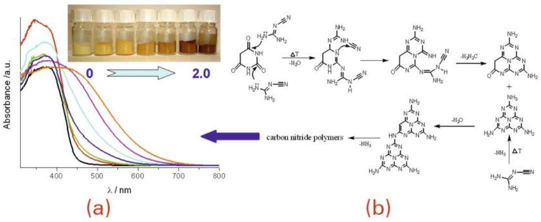

Fig. 1: Light absorption of new carbon nitride structure (a) and the proposed copolymerization processes of dicyandiamide with barbituric acid (b). Inset (a) is the picture of new carbon nitride samples

Synthesis of SBA-15-Type g-C_3N_4

To increase the photocatalytic activity of g-C_3N_4, nanosized pores have been created in bulk g-C_3N_4 to enlarge its external surface area **[4]**. Using mesoporous silica (SBA-15) as a hard template, a rod-like ordered mesoporous g-C_3N_4 (ompg-C_3N_4) was obtained, see **Fig. 2**. Ompg-C_3N_4 possesses a large surface area (239 $m^2.g^{-1}$), uniform pore size, and a 2D accessible framework. The hydrogen evolution rate of this nanoporous C_3N_4 was five times higher than that of bulk g-C_3N_4. **[5]**

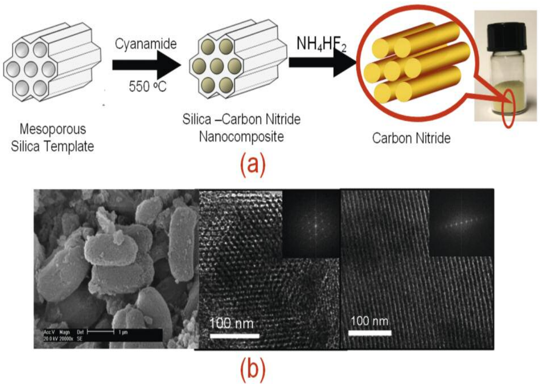

Fig. 2: Pathway for the synthesis of ompg-C_3N_4 (a) and its SEM and TEM characterizations (b).

Sulfur-Mediated Synthesis of g-C_3N_4

Classic C_3N_4 solids are prepared by the bulk condensation route using nitrogen-rich monomers (e.g., cyanamide, melamine, and melem) containing –NH_2 motifs as the leaving groups during the polycondensation. This bulk deamination reaction, however, suffers from incomplete polymerization due to kinetic problem. We have demonstrated that using amino-group-free trithiocyanuric acid as precursor where the –SH groups act as the leaving groups to synthesize carbon nitride (CNs) can offer an effective approach to modify its texture, optical and electronic band structure properties, as well as the photocatalytic activity, see **Fig. 3**. The water splitting reaction has been achieved at a moderate rate with bare C_3N_4 without using co-factors. **[6]**

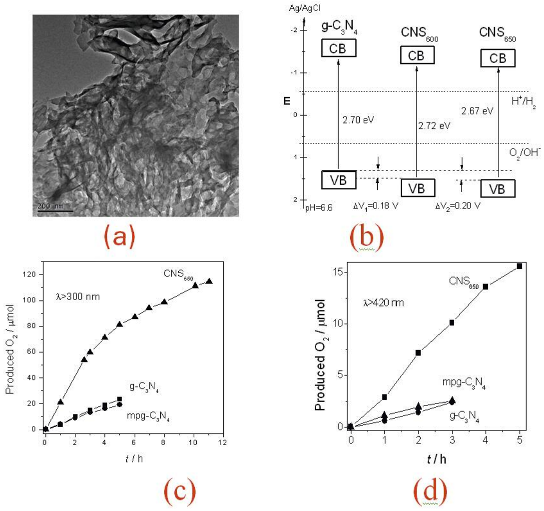

Fig. 3: A typical TEM image of C_3N_4 synthesized by a sulfur-mediated approach (a) and electronic band structure of classic g-C_3N_4, CNS_{600} and CNS_{650} (b). Oxygen-evolution by g-C_3N_4, mpg-C_3N_4 and CNS_{650} as a function of time under UV (c) and visible light illumination (d).

Heterogeneous Organophotocatalysis

We analyzed the electronic band structure of g-C_3N_4 by electrochemical methods. Results revealed that the conduction band (CB) and valence band (VB) of g-C_3N_4 are located at -1.3 V and +1.4 V vs. NHE, respectably **[3, 6]**. Light-excited electrons in the CB of g-C_3N_4 possess a large thermodynamic driving force to reduce O_2 ($E^{o'}(O_2/\bullet O_2^-)$ = -0.16 V), but the potential of the photogenerated hole in the VB is inadequate to oxidize -OH to /•OH ($E^{o'}$(-OH/•OH) = 2.4 V), see **Fig. 4a**. These features provide an argument that g•-C_3N_4 might act as a suitable candidate for photooxidation and related transformations. g-C_3N_4 was therefore chose as a organocatalyst for selective oxidation of alcohols **[7]** and oxidative coupling of amines **[8]** using molecular oxygen and visible light, see **Fig. 4**.

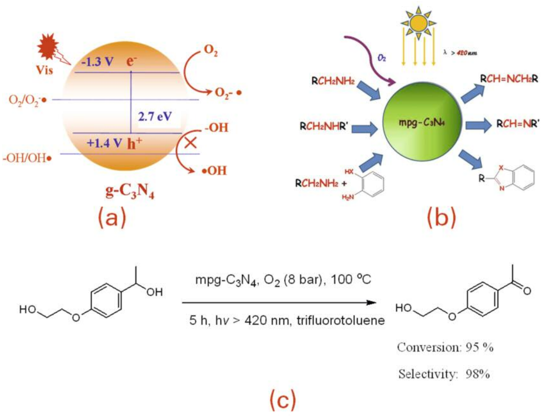

Fig. 4: Electronic band structure of g-C_3N_4 (a). Selective oxidation of alcohols (b) and oxidative coupling of amines (c) photocatalyzed by carbon nitride.

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