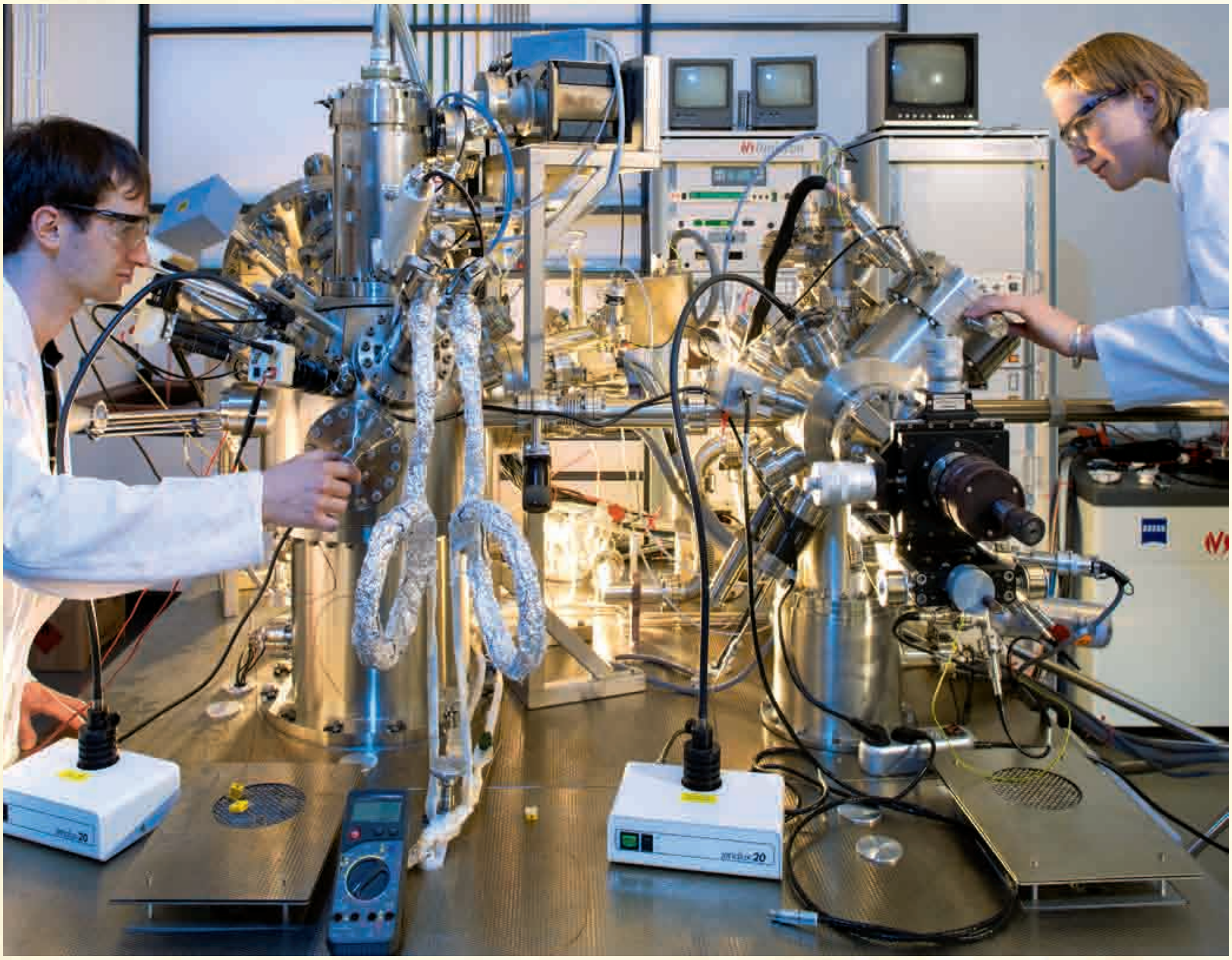
From Molecules to Materials

Cluster of Excellence “Engineering of Advanced Materials – Hierarchical Structure Formation for Functional Devices”



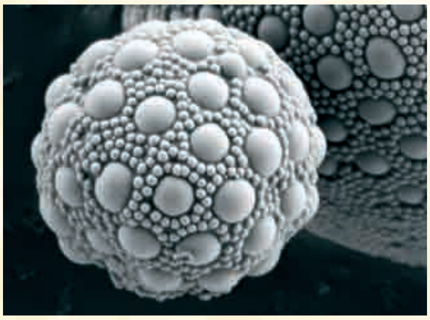
Research on systematically creating nanostructures on surfaces is conducted in ultrahigh vacuum.

Scientific Objectives

Advanced materials with properties tailored on the molecular and meso scales are expected to stimulate evolutionary advances and revolutionary breakthroughs in emerging key technologies such as information and communication technology, catalysis, energy, and transportation. Hence, the ability to design novel materials and processes will have a strong impact on ensuring industrial competitiveness, economic growth and a better quality of life. Based on the unique combination of the top-ranked Faculties of Engineering and Natural Science at the Friedrich-Alexander University of Erlangen-Nürnberg, the scientific concept of the Cluster of Excellence “Engineering of Advanced Materials – Hierarchical Structure Formation for Functional Devices” (EAM), which was established in November 2007, focuses on the science and engineering of hierarchical materials organized from the molecular to the macroscopic levels.

The vision of the Cluster of Excellence is to close the gap between fundamental research and real-world applications of modern high-performance materials in key scientific and engineering areas. Bridging the gap between materials design at the molecular level and macroscopic properties (“from molecules to materials to functions”) requires the development of novel approaches capable of covering an extensive range of time and length scales in modeling and simulation, processing and manufacturing, and structure, property and process analysis.

In a coherent methodological approach, the following cross-sectional topics are investigated:



Colloidal crystals: the Cluster examines how ordered structures with special optical properties can be fabricated from particles.

- Particle technology (Prof. Wolfgang Peukert)
- Nanoanalysis and electron microscopy (Prof. Mathias Göken)
- Multiscale modeling and simulation (Prof. Günter Leugering, Prof. Tim Clark)

The functional-material aspects are organized in value chains that represent hierarchical material classes with increasing complexity, including

- Engineering of nanoelectronic materials (Prof. Andreas Hirsch)
- Engineering of photonic and optic materials (Prof. Philip Russell, Prof. Ulf Peschel)
- Engineering of catalytic materials (Prof. Peter Wasserscheid)
- Engineering of lightweight materials (Prof. Robert Singer).

These seven topics form the research areas of EAM. The coordinator of the Cluster is Prof. Wolfgang Peukert, Institute of Particle Technology, who initiated the proposal within the Excellence Initiative, which was initiated by the German Federal and State Governments under the supervision of the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation).

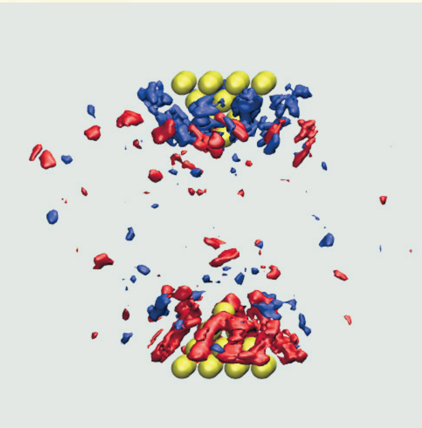
New paths are being forged in cooperation with non-university institutions and industrial partners. Two Fraunhofer Institutes (Integrated Systems and Device Technology (IISB) and Integrated Circuits (IIS)), the Max Planck Institute for the Science of Light, the Bavarian Laser Center (BLZ) and the Bavarian Center of Excellence in New Materials are tightly associated. Together with partners from industry, they are united in developing new products organized in process chains that simultaneously catalyze interdisciplinary research and create highly relevant innovation with the potential for large economical impact. The motto is: innovation occurs at the interfaces.

Coherence of Methods

Despite the large diversity of applications, the concepts of materials and process development are geared to common principles. Molecular materials, particle technology, analytical tools and methods, and multiscale (both temporal and spatial) modeling and simulation are research areas of central importance to all areas of EAM. They are therefore organized in interdisciplinary research centers. Their overall goal is to develop common methods for fabricating building blocks (molecules and particles) that are required for formatting structures in the other research areas.

An Interdisciplinary Center for Molecular Materials was founded as early as 2006. It was expanded within the framework of the *“Bayerischer Innovationsfonds”* and will be integrated into EAM’s activities.

In the new Center for Particle Technology, novel methods for particle fabrication, formulation, and characterization will be developed. The vision is to provide a ‘library’ of different types of particles with controlled size, shape and internal morphology. It is essential that the fabrication



Molecular dynamics simulation of an ionic liquid between two gold nanoelectrodes (yellow). The simulation shows one layer of anions (blue) at the cathode (top) and a corresponding layer of cations (red) at the anode (bottom). The formation of a double layer at the cathode is clearly visible. For very short distances a vacuum region forms between the electrodes. This is occupied by molecules of the ionic liquid only for larger distances. These simulations explain the exceptional behavior of ionic liquids in “break junction” experiments.

EAM documents the outstanding expertise and international visibility of research at the University of Erlangen-Nürnberg in the fields of materials and processes. The scientists involved have a high international reputation, and three principal investigators are Leibniz Awardees.

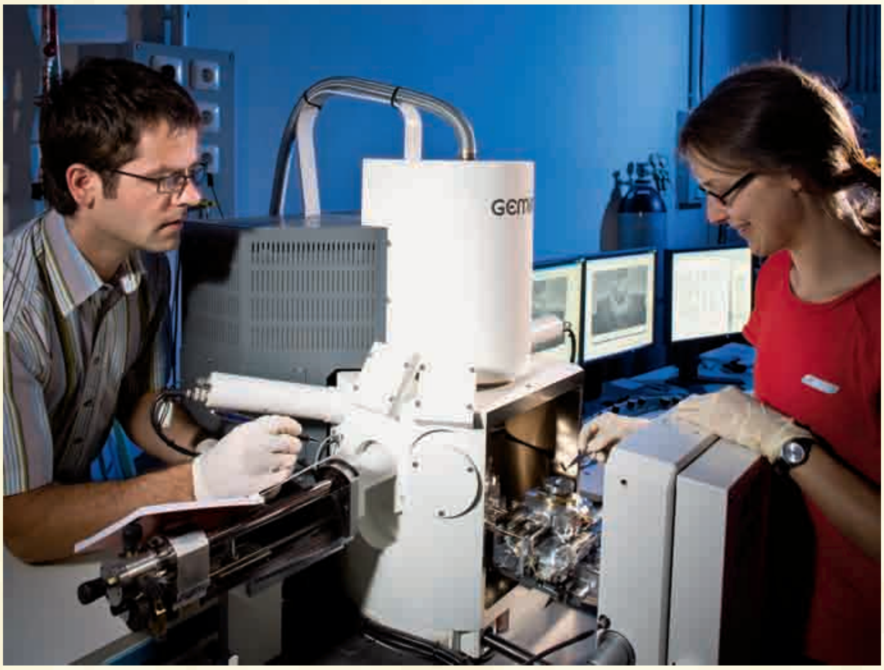
Modern challenges in science and engineering call for new types of interdisciplinary cooperation between the researchers involved as well as new forms of organizational structures. EAM combines the following eight disciplines: Applied Mathematics, Chemical Engineering, Chemistry, Computer Science, Electrical Engineering, Materials Science and Engineering, Mechanical Engineering, and Physics.

Filling a cryostat with liquid air. In this apparatus silicon-carbide transistors for high-power electronics are examined.

of the building blocks in sufficient quantities is possible, even under industrially relevant conditions. From these building blocks, multifunctional structures are assembled by innovative processes, providing the basis for new products with high added value. The market volumes of the related applications are often huge, the market for printable electronics, for instance, is estimated to be some 10 billion Euros. To strengthen the Center for Particle Technology, a new professorship for particle synthesis has been established within the framework of EAM.

Particles, structures and new materials are characterized along the whole process chain in the new Center for Nanoanalysis and Electron Microscopy (CENEM). Besides high-resolution electron microscopy with atomic resolution, *ex situ* and *in situ* scattering and spectroscopy methods are being developed and made available to the whole Cluster. For this task a new, state-of-the-art transmission electron microscope (TEM) has been acquired. This TEM with field emission cathode and aberration correction enables sub-nanometer resolution, imaging of the atomic structure with excellent clarity and chemical analysis along interfaces. Fascinating new microscopy techniques allow *in situ* deformation of microscopically small samples inside the TEM, making changes under load directly visible. Furthermore, tomographic image reconstruction by tilting the sample and inspection under different viewing angles has recently become possible, even in the TEM. This is important for recording the full 3-dimensional structure of materials and particles on the nanoscale. This key area will be supported by two new professorships for electron microscopy and nanomaterial characterization by diffraction and scattering methods.

The newly founded Center for Multiscale Modeling and Simulation (CMMS) works on multiscale approaches and methods for structure, property, and process optimization. The research concept connects quantum mechanical approaches on the molecular scale to discrete approaches for particle systems and to methods of continuum mechanics. As the core of the new center, a new chair on multiscale simulation of dispersed systems has been established. The CMMS builds on the university's unique expertise in the fields of theoretical and computer chemistry, theoretical physics, materials science, and chemical engineering/fluid mechanics, together with the fields of numerical methods and modeling from applied mathematics, and high-performance computing.



Mounting a graphite nano-transistor in the high-resolution scanning electron microscope.

Range of Applications

Nanoelectronic Materials

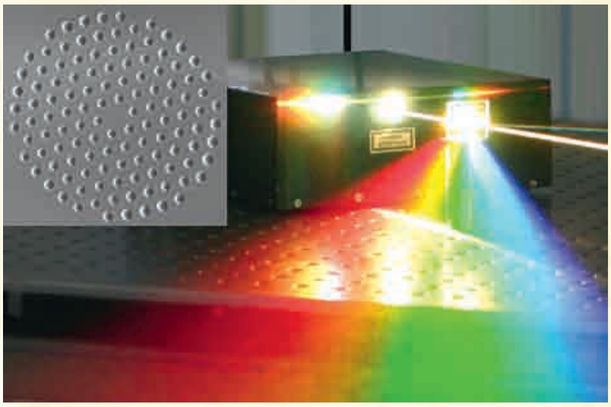
In the context of mass-market consumer products with restricted profit margins, alternative approaches to classical silicon technology for nanoelectronics are now in demand. For this purpose, new functional

Fabrication of photonic crystal fibers.

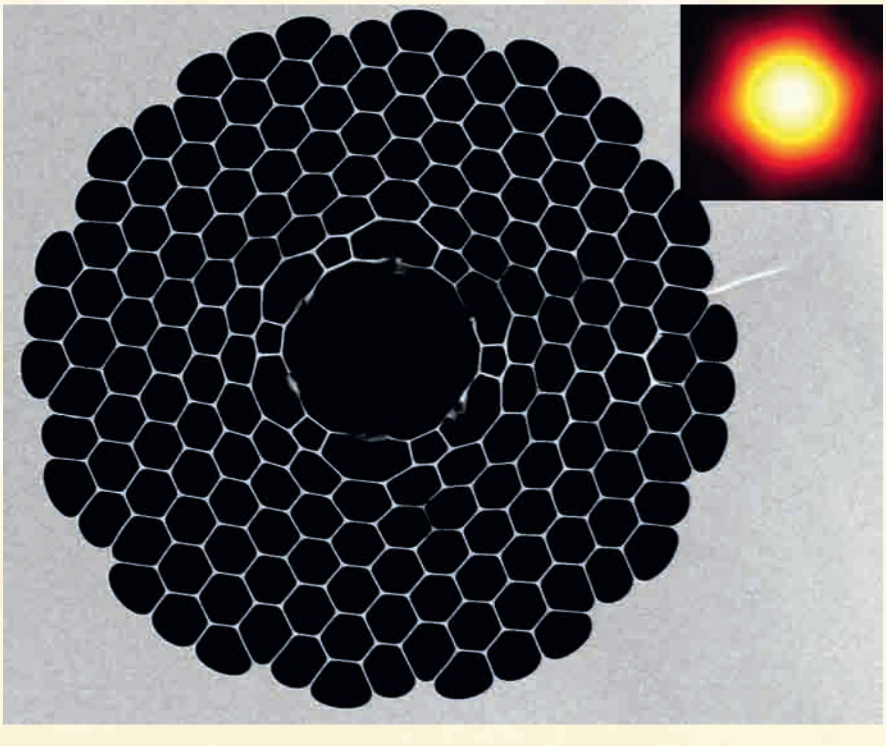
A stack of glass rods and tubes as preform for drawing fibers.

materials constitute a powerful solution and play a key role. This is where EAM intends to make significant contributions. In particular, research into materials for nanoelectronics concentrates on new concepts for the realization of low-cost and powerful electronics for future applications. Such an approach significantly contrasts the developments linked to classical silicon-based micro- and nanoelectronics. Two major prototypes of materials, including their engineering into ordered structures and devices, are being investigated. On the one hand, electroactive organic molecules and on the other hand inorganic nanoparticles are being used as fundamental building blocks. In both areas, the Erlangen researchers have demonstrated broad and in many ways world-leading expertise. Research in molecular and polymer-based electronics deals with visionary electronic devices assembled from single organic molecules to wires or logic circuits.

The production of an organic solar cell as a demonstrator with the potential for market entry is conceivable in the medium term. In particular, the application of new molecular carbon allotropes like fullerenes or carbon nanotubes is actively promoted. Particulate-based electronics combine the advantage of polymers – being applied on flexible substrates – with the stability of classical silicon technology. They are characterized by longevity, stability, and reliability. Fundamental questions include the electron transport across particle interfaces, the self-organization of semiconducting nanoparticles in thin layers, and their integration into functional devices. The main technological challenge is to demonstrate the construction of basic electronic circuits from printable nanoparticulate pastes. Even at this early stage of the cooperation within EAM, very promising results have been obtained through intensive collaboration of the scientists involved. They have, for example, succeeded in coating inorganic nanoparticles with a thin layer of carbon units, thus providing the precondition for electronic interaction between hierarchically ordered particulate structures.



White-light produced by photonic crystal fiber (cross-section see inset) radiates 100,000 times more brightly than the brightest incandescent lamp.



Cross-section of a hollow-core photonic crystal fiber, inset: mode profile of the light guided in the fiber.

Photonic and Optical Materials

The performance of conventional optical devices is limited by the properties of the materials from which they are constructed. The success of the optics industry in the second half of 19th century was enabled by use of new glasses, and today optical lith–ography, one of the key technologies in the production of semiconductor microchips, depends strongly on the availability of a broad range of optical materials. In the past, one essentially relied on chemical methods for finding new base materials. Recently, the rapid development of nanotechnology enables completely new possibilities for nanostructuring.

One can, for example, already manufacture artificial ‘atoms’, i.e. units with sub-wavelength dimensions. By making clever use of resonance effects, the coupling to the electrical field can be modified in the desired way. Such designed basic units are then assembled into macroscopic materials – metamaterials, as they are called. Although similar concepts have been demonstrated previously, and first experiments have given us an idea of the great potential of this vision, there is still a long way to go until the concept can be realized. In particular, the sheer number of quasi-atoms required to form macroscopic metamaterials poses a great challenge. Within the framework of EAM production and controlled agglomeration of exactly determined, optically active nanoparticles are used to produce completely new materials in macroscopic quantities. For example, dielectric particles are specifically coated with metallic layers in order to achieve special color effects, or the magnetic response of macromolecules in the visible spectral region is examined. Ultimately, the full path from design of individual basic components through the specific alignment of 3-dimensional metamaterials to the construction of operational optical components will be demonstrated.

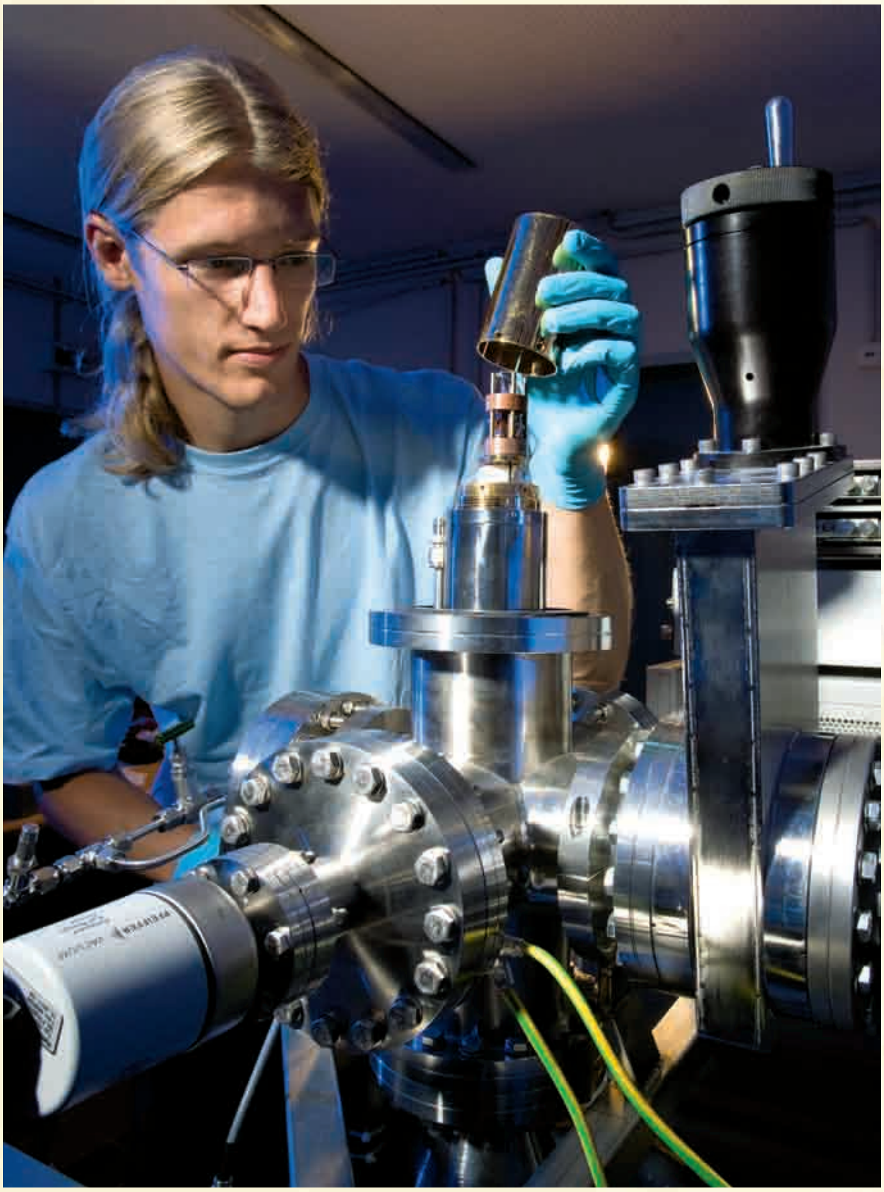
A further impressive example for the successful application of micro- and nanostructuring are photonic crystal fibers (PCF). Their design, fabrication, and application are one of the objectives of the Cluster. Photonic crystal fibers are glass fibers with a cladding that is penetrated by microscopic channels along the longitudinal direction. In cross-section, these channels form a periodic hole pattern which lends these fibers exciting light-guiding properties. The regular pattern of micro- or nanoscopic glass rods and tubes acts on the light as a 2-dimensional crystal which concentrates the light in a central wave-guiding core. In recent years, PCFs have revolutionized non-linear optics and have opened completely new fields of application. However, their potential is far from being fully exploited. Compared to conventional glass fibers, the properties of PCFs can be adjusted using a broad range of parameters. This enables for instance nearly perfect adaption to particularly efficient frequency conversion. Furthermore, chemical substances and particles can be introduced for examination into the cavities present in PCF, where they interact with light. This leads to new possibilities for sensing or analysis of tiny amounts of material. One research goal of the Cluster is to realize chemical reactions within the micrometer-sized PCF cavities with parallel monitoring by fiber-guided radiation ('lab-in-a-fiber').

To achieve this goal, scientists from physics, chemistry, mathematics, and process engineering must collaborate closely. This prerequisite is fulfilled within the Cluster of Excellence in an ideal way.

Catalytic Materials

Catalysis is the key technology for the sustainable production of chemicals and an important tool for manufacturing high-performance materials (e.g. polymers and their raw materials). Most transformations and reaction processes in the chemical and related industries benefit from catalysis; 90% of all chemicals come into contact with at least one catalyst during their manufacturing process. Catalysis is a broad interdisciplinary field. It comprises the different approaches of heterogeneous and homogeneous catalysis and biocatalysis. The ultimate goal in catalysis research is to combine the selectivity and specificity of a biocatalyst with the robustness and synthetic availability of homogeneous catalysts and finally the ease of processing that is offered by a heterogeneous catalyst. To realize this vision, the strategic collaboration of chemists, spectroscopists, chemical and bio-engineers, and materials science engineers is essential. The required competencies span the range from molecular design and computer chemistry to preparative organometallics, from inorganic solid state chemistry to surface science, from spectroscopy to chemical vapor deposition, from particle technology to reaction engineering and from bio-inspired catalyst design to bio-mimetic structural architectures. All the expertise required to implement such a strategic research effort can be found at a very high international standard in Erlangen.

EAM concentrates the existing expertise and areas of excellence on joint targets and focuses on the development of novel catalysts for special, technically relevant applications from the group of selective C-C-coupling and -cleavage reactions. For these applications, the full research chain from the design of individual catalytic centers on the molecular level to an almost technical, pilot-plant scenario will be established. This concept includes focused research activities in materials synthesis, analytical methods, system integration, materials production and catalyst testing. The scientific output from this multiscale approach, which bridges the traditional gaps between classical research areas, is expected to be of great general relevance, well beyond the selected demonstrator applications. In this way, an extremely inspiring environment for cutting edge research in catalysis evolves that will result in substantial scientific impact and great visibility.



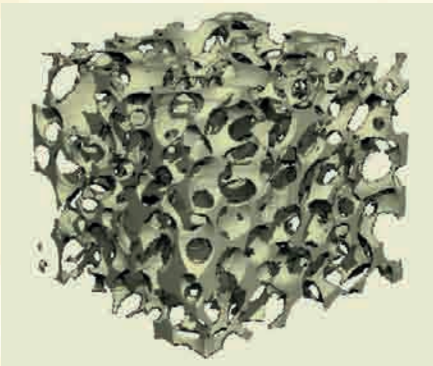
Preparations to contact a single organic molecule.

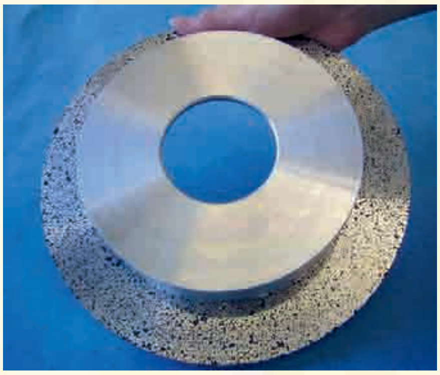
Lightweight Materials

Cellular, foam-like materials with nanoscale microstructure for the design of low density but high strength components in transportation are explored. Reducing energy consumption and emissions but increasing the engine efficiency of future automobiles can only be achieved if novel materials of lighter weight but higher strength, toughness and flaw tolerance become available. Localization of micromechanical deformation and fracture processes due to cellular macrostructure and atomic structure of interphase boundaries is a great challenge in developing strengthening concepts and adequate processing and fabrication techniques. The processing chain includes materials processing, based primarily on generative techniques, and microstructure optimization supported by model-based simulation approaches. As demonstrators with high innovative potential in automobile technology, multifunctional exhaust gas purification devices for minimizing emissions and highly loaded structural components are being developed.

During the first phase, research is concentrated on the development and structural optimization of cellular ceramics and metals, metal/ceramic and polymer/ceramic composites, which are produced from macromolecular precursors and melts by foaming processes. In cooperation with the Center for Multiscale Modeling and Simulation, the cellular structure is optimized in order to improve the mechanical properties significantly. Questions about cell structural mechanics and the influence of graded and multilayer nanoscale cell wall structures on the deformation and fracture behavior lie at the focus of experimental examinations and atomic-level *ab initio* calculation methods.

In the second phase, the design approaches which in the first phase were focused on isotropic and homogenized cellular materials will be extended to structure models characterized by a hierarchical architecture. The anatomy of cellular tissue structures adopted from evolutionarily optimized biogenetic materials serves as a template for novel biomorphous materials with a hierarchical architecture that is adapted to the local stress in the device.





X-ray micro-CT image of a polymer-derived ceramic foam (left) for locally strengthening light metal constructions (right).

Honeycomb structured as well as dense cellular materials are constructed by periodic arrangement of building blocks with dense-packing polyhedral shape. The decoupling of the property optimization in the individual building block (cell) and the global behavior of the periodic cell arrangement (tissue) marks a paradigm shift in the development of new properties and functions of future high-performance materials. Filling periodic honeycomb structures with a metal or a polymer leads to novel, interpenetrating phase composites that show adaptive and responsive behavior. Biomorphous materials that are capable of regenerating from utilization-caused damage by crack healing can enable a breakthrough in the design and application of high-performance materials with improved lifetime and safety (self-healing materials).

Promotion of Young Researchers
EAM aims to take a pioneering role in developing and realizing new concepts for the promotion of young researchers. Young scientists are promoted in a multilevel scheme starting at the high school level, up to the graduate, and post-graduate to the leadership of independent junior research groups. At the first level, it builds on the existing strong activities of the University of Erlangen-Nürnberg (e.g. road shows with trial studies, mobile experiments inside a “faculty in a suitcase”, annual girls-engineering practical courses, a week-long “girls and technology internship”, and university for youngsters j-uni). Key elements of the second level (undergraduate students) are learning-by-experiencing, conducting research as early as possible, establishing state-of-the-art lab courses including high end equipment (e.g. pilot-plants).

Based on the outstanding density of top researchers and teachers, the overall aim of graduate promotion (the third level) is to create attractive conditions for doctoral studies in order to motivate the best graduates to enter a doctoral program at the University. The establishment of the new Graduate School Advanced Materials and Processes also guarantees a high quality of education and mentoring within the framework of EAM. The Graduate School is organized into eight interdisciplinary classes that will collaborate closely with existing activities in Erlangen such as the Graduate School in Advanced Optical Technologies (SAOT) and the International Max Planck Research School for Optics and Imaging (IMPRS-OI).

The Graduate School Advanced Materials and Processes will offer comprehensive opportunities for the education and personal development of doctoral students. Depending on their interests and specialization, the students will be prepared optimally for a career in industry or academia. Interdisciplinary lecture courses, a Science-to-Innovation-to-Business competition to promote transfer capabilities of fundamentals to application, summer/winter schools and various seminars including ones given by highly ranked scientists and industrial leaders will be offered. Additional elements are the integration of leadership skills, deepened international experience by exchange with highly ranked partners worldwide and conference visits. These will all be strengthened by the activities of the Cluster. In December 2008, an international workshop with leading universities from Switzerland, USA, Japan, Australia and China was organized.

In its Rising Star Program EAM provides attractive leadership positions for highly promising candidates at the post-graduate level. The fellows of the program are awarded resources to establish independent research groups at an early stage in their careers. In this way, they are given the chance to develop and establish themselves in a multidisciplinary and highly stimulating atmosphere. Moreover, these candidates can benefit from free access to all the facilities, equipment and services EAM offers.

In order to attract excellent young scientists to the Cluster and to promote visibility and international reputation, a highly ranked research award (Erlangen Excellence in Materials Engineering Award) will be granted. The awards will support outstanding researchers with 750,000 Euros to concentrate on high-level, innovative research of their own choice but in cooperation with, and within the framework of EAM. The award will allow financing new research groups and stimulate new collaborations.

Transfer of Results from Fundamental Research to Applications
Successful technology transfer is an important goal of the Cluster. Two structural elements have been developed within the framework of EAM: the Incubator Program to promote research-intensive start-up companies, and the Industrial Liaison Program.

The Incubator Program is dedicated to providing an ideal environment for technology-based, commercial, spin-off activities arising from the fundamental studies carried out in EAM. It will concentrate on providing assistance, especially during the seed and start-up stages, which are the most critical for success.

Promotion of young researchers is a central mission of the Cluster and prepares for careers in academia and industry. The picture shows a junior scientist examing an ultra-thin electronic device.

abroad, thus creating additional visibility and attracting the best young scientists to Erlangen.

A dedicated fund for promoting *gender equality* has been allocated. With these resources, measures will be initiated to improve reconciliation of scientific career and family life further. These measures build on existing activities of the University. Furthermore, an incentive system has been created that rewards the employment of young female scientists. Other measures will be developed within the framework of an ideas competition.

EAM perceives itself as an experimenting field for new approaches and structures that will change the University as a whole. One example is the first appointment of a new chairholder within EAM, which was achieved within four months from advertisement of the position to the decision of the search committee. Such a fast procedure was made possible by close cooperation of the faculty, the central university administration, and the Cluster. In this procedure, a three day colloquium was held, during which all candidates presented their work to an audience from EAM and University. This new form of candidate selection led to an intensive exchange between everyone involved. It offered the candidates the possibility to inform themselves about EAM and its activities, and there are already indications of further cooperation emerging from this basis.

The Industrial Liaison Program builds on the Faculty of Engineering's traditionally close liaison with industry by providing a direct link between materials science, engineering and processing research at the University and the needs of the industrial partners.

Considering the companies' different sizes, interests and financial power, a three step gradual model of cooperation has been developed that ranges from analysis of the strengths and weaknesses of potential industrial partners (industrial affiliate forum), bilateral cooperative projects to answer individual research questions (preferred partnership) to strategic alliances on interdisciplinary topics initiated by industry (strategic partnership). Strategic alliances are of special interest and will be conducted with selected partners. A prerequisite for those alliances is that fundamental scientific questions are addressed that must be solved in order to establish highly relevant new technologies with potentially large economical impact. Major companies have decided to enter strategic alliances and preferred partnerships. Examples for cooperation comprise the development of new optical materials (BASF), new catalytic materials (Südchemie), or materials for printable electronics (POLYIC). According to the special scientific interest and the required mutual transfer of results between partners additional funds are allocated by the Cluster. The larger financial basis allows interdisciplinary teams specifically tailored to the scientific questions to be formed. This measure will help to overcome most barriers to scientific advance. The huge interest of industry in this structural instrument shows that there is large demand for novel, unconventional but straightforward solutions.

Structured Measures to Catalyze Excellence Further

In the *Ambassador Program* officially retired colleagues with exceptionally high visibility will be given the possibility to continue aspects of their research in areas of high relevance to EAM. These colleagues will not only help to guarantee continuity in research excellence, but also will serve as ambassadors for the Cluster on the national and international levels. Above all, they will use their personal academic networks to advertise the Cluster and its special opportunities to colleagues from universities

Structural Integration of the Cluster of Excellence

EAM was established as a central institution of the University. This fact reflects the significant importance that is attributed to its activities as the only Cluster of Excellence at the University of Erlangen-Nürnberg and in Northern Bavaria: responsibility for EAM is directly assigned to the University's executive board of management. The Cluster acts as an important pillar of the University's research focus 'Materials and Processes' and further strengthens and expands this focus. At the same time, the establishment as a central institute forms the basis for a continuation of EAM's activities, securing the sustainability required by DFG within the framework of the excellence initiative.

The Cluster's executive board consists of the coordinator Prof. Wolfgang Peukert, the co-coordinator Prof. Peter Wasserscheid, and the coordinators of the individual research areas, as well as a representative of the scientific staff. A women's representative has been appointed to ensure equal treatment and equal opportunities for men and women working at EAM.

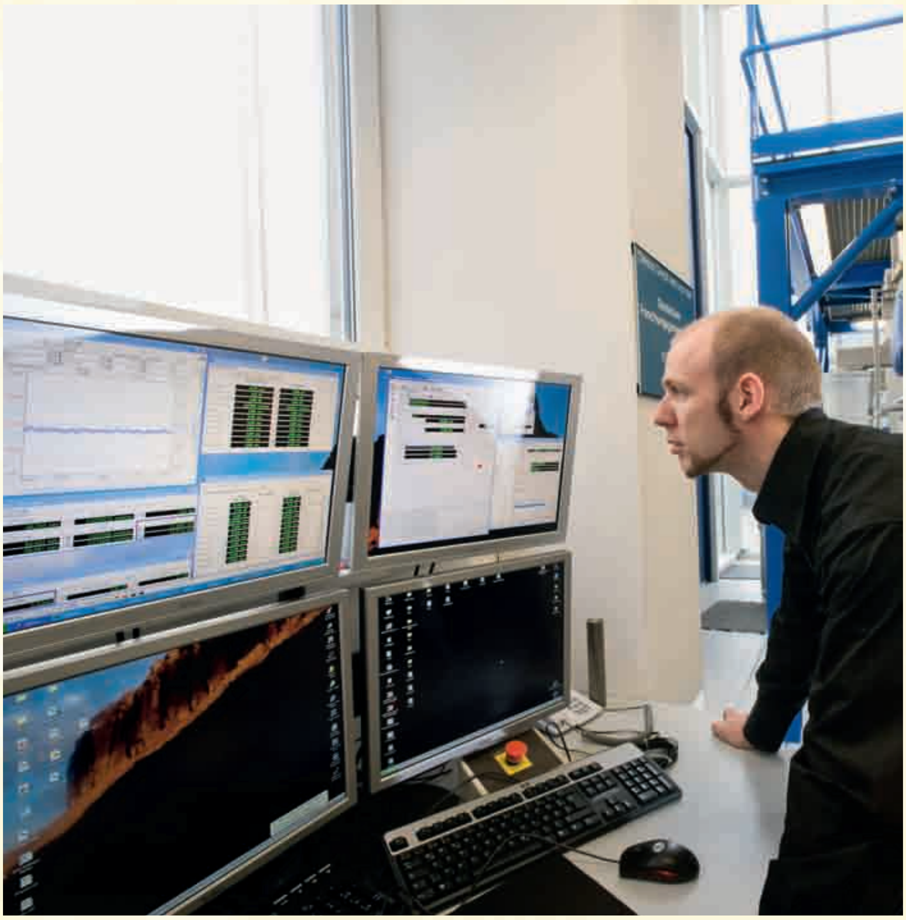
An advisory board consisting of high-ranking experts from science and industry that are internationally renowned in EAM's research fields supports the executive board. In particular, its task is to give suggestions and to make statements regarding the scientific and structural development of the Cluster, as well as to take an active role in quality assurance.

EAM is supported by a professional administration that deals with the financial and organizational aspects of the Cluster's activities and which relieves the scientists of administrative tasks to a large extent. One important aspect is the organization of workshops and conferences, which cross-link the individual research areas with each other and with scientists worldwide. The EAM administration is responsible for implementing the individual programs (e.g. technology transfer), the international exchange with other research institutions, and last but not least for the Cluster's internal quality assurance. For these tasks, EAM was able to win the former head of the executive staff of the University management, who coordinated the activities in the excellence initiative during the application phase. With her knowledge of the proposal and of the University structures, she dynamically supported the set-up of the Cluster activities. EAM benefits from support by a dedicated PR manager, who is responsible for the internal and external communication related to EAM. She contributes to its improved national and international visibility in the public and in the scientific community. Besides that, she is also responsible for collaborations with schools with the aim of interesting pupils for the topics of the Cluster at a very early stage and to inspire them to look into scientific and technological questions.

Sustainability of the Activities

In order to realize its activities within the framework of the excellence initiative, the Cluster will receive a total of approximately 40 million Euros funding from the DFG (including the program overheads). Additional, important contributions come from the University and the Bavarian state and German federal government. On the University's south campus, several projects are underway: besides an already completed building for the new TEM, a new building for an Interdisciplinary Center for Functional Particulate Systems (which will also house a part of EAM's activities in the field of optics) is under construction, the chemistry technology hall in Egerlandstraße will be renovated and extended. For these buildings, the Cluster will receive 18 million Euros from the 'BayernFIT program' and 4.5 million Euros from the federal government. In this way, a valuable contribution has been made to securing the sustainability of EAM. Additionally, the University has promised continuation of all new professorships created from funds of the excellence initiative. In this process, the tenure track for junior professorships has been realized for the first time within the framework of EAM. Again, the Cluster can act as pioneer within the University.

Images: EAM, Erich Malter, MPRG



In the extended view scanning electron microscope (XV-SEM), large devices can be inspected for tiny material faults non-destructively. Unrivaled worldwide is its extremely large specimen chamber. With a volume of 2 cubic meters it offers enough space to examine complete turbine blades, crankshafts, or cylinder heads.

E A M ENGINEERING OF ADVANCED MATERIALS

Coordinator:
Prof. Dr. Wolfgang Peukert
Email: w.peukert@lfg.uni-erlangen.de

Friedrich-Alexander University of Erlangen-Nürnberg
Cluster of Excellence
Engineering of Advanced Materials
Nägelsbachstraße 49b
91052 ERLANGEN, GERMANY

Phone: +49.9131.85.20846
Fax: +49.9131.85.20848
Email: administration@eam.uni-erlangen.de

Date of publication: Summer 2009