

Current information from the Materials Science and Technology Institution of the ETH Domain, Switzerland

From the surface physics of lily ponds to nanotechnology

Focus

On the trail of molecular self-assembly

Researchers in the nanotech@surfaces laboratory are using the analogy of water waves on pond surfaces and electron waves on metal surfaces to learn more about the interactions between adsorbed molecules and surfaces. This knowledge may help to better understand the self-organizing nature of molecules. Molecular self-organization could in turn aid in the generation of nanostructures on surfaces.



■ MARTINA PETER, PIERANGELO GRÖNING

Who hasn't at one time or another sat dreamily on the banks of a pond on a quiet summer evening and observed the complex patterns formed by delicate waves reflected from the banks, reeds and lily pads? These wave patterns, which appear so complex, are defined in completely prosaic terms by the wavelength of the water wave as well as the geometry and positions of the scattering centres (such as the edges of the lily pads) which reflect the waves. The wave patterns – and this is where the researchers become interested – can also be used to draw inferences regarding the geometry and distribution of the scattering centres.

Waves on the electron pond

Metals possess free electrons which are not permanently bound to individual atoms, but rather can be associated with the entire solid. The states of these electrons form a type of pond, on the surface of which, in the case of certain metals, waves similar to those on the lily pond can form. Viewed in a scanning tunnelling electron microscope (STM), the wave trough stands for a low electron density and the wave peak for a high electron density. The amplitude of the electron density waves on the copper surface is 5 picometres (10^{-12} m), which just corresponds to one fortieth of the diameter of a copper atom.

Molecular self-organization

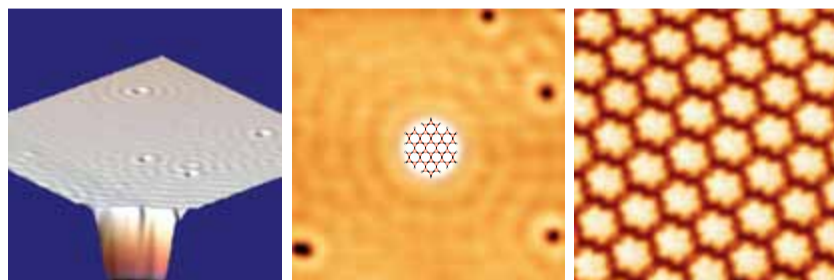
Empa's surface physicists see molecular self-organization as a highly promising approach to the generation of new types of

nanostructures on surfaces, using molecules as the building blocks. In the same way as in nature, a small number of molecular building blocks should grow to form complex supramolecular structures which will one day perform specific electronic or optical functions. In order to be able to make controlled use of molecular self-assembly it is first necessary to investigate and understand the interaction between the molecular building blocks and the substrate surface. As was illustrated, one way to discover the interaction of an adsorbed molecule with a surface is to study the wave pattern of the electrons in the vicinity of the adsorbed molecule. This wave pattern tells researchers which parts of the molecule are interacting with the surface. Like the lilies, the molecular orbitals reacting with the surface dip into the pond, acting as scattering centres for the electrons. Computer-simulated scatter patterns can be used to draw inferences from the measured wave pattern about the locations of the scattering centres and thus about the interaction points of the molecule with the surface.

However, the electron waves can also trigger a repulsive effect between the molecules. The higher electron density around the molecule acts as a buffer. At lower molecular coverages, this prevents one molecule from coming too close to another. As a result, the disc-like molecules of 42 carbon atoms known as hexabenzocoronene (HBC) do not organize into a regular pattern until a specific critical coverage is reached and the molecules press each oth-

er onto the surface. Below the critical coverage level, the molecules are mobile and do not form any organized structures. ■

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Left: CO molecules adsorbed on a Cu surface act as scattering centres for the electrons on the surface. The atomic step in the foreground ($h = 0.2$ nm) indicates how small the amplitude of the electron wave is. (3D representation from a STM micrograph, 30×30 nm²).

Centre: Cu surface with an adsorbed HBC molecule (outlined) and 4 CO molecules (STM micrograph, 13.5×13.5 nm²).

Right: Perfectly ordered HBC molecules on a Cu surface (STM micrograph, 10×10 nm²).

This Empa work on molecular self-assembly is financed by funding from the 6th EU Framework Programme. Empa is responsible for the scientific and organizational management of the STREP Project «RADSAS». Partners in this work are the Max-Planck Institute for Polymer Research in Mainz and the Surface Science Research Centre of the University of Liverpool.

Editorial



Benefits for the economy, education and culture

Science and technology on the smallest scale – in the micro and nanometer range – is crucial for a high-tech country like Switzerland. Institutes of technology, universities of applied science, public and private research organizations and industrial bodies are all becoming increasingly involved in this area, so is the Empa.

Read about the innovative work being done within our «Nanotechnology 2» research program in this edition of the empaNews. We report on molecular self assembly, the construction of an ultra high-vacuum force microscope, equipment developed together with the PSI for structuring the surface of synthetic fibers, and the melt spinning plant for bicomponent fibers.

We work on different topics, in an interdisciplinary manner and within international networks. Our highest priority is to ensure that economy, education and culture benefit from our activities.

Louis Schlapbach

Louis Schlapbach, CEO Empa

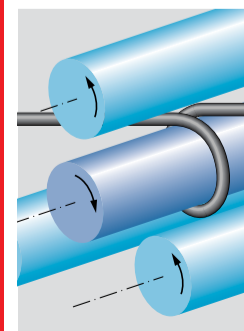
See next pages

3 ■ 2004



Page 2

A sophisticated, ultra-high vacuum force microscope is currently being developed and constructed at the Empa.



Page 3

The Empa has developed an embossing system with which the surface of individual fibres can be given a defined structure.

Development prize rewards efforts

At LÖT 2004 – 7th International Conference on Brazing, High Temperature Brazing and Diffusion Bonding, Dr Ulrich Klotz of the Joining and Interface Technology department presented a paper entitled «Interface reactions between diamond and active brazing filler metals» on behalf of a team of researchers¹. The organizers of Europe's most important conference in this field awarded the project the second of six development prizes. An essential contribution to this work was made by Prof. Fazal A. Khalid, on sabbatical leave from the GIK Institute of Engineering Science and Technology, Pakistan. The results achieved form the basis of an SNSF-funded project that is investigating and modelling phase diagrams and interface reactions during the active brazing of diamond. Among other things this work has technological relevance for new high-performance abrasive tools which the department is developing jointly with ETHZ and industrial partners. The award confirms the validity of the strategic decision to concentrate on developing the «CALPHAD» modelling area at Empa. Further intensive work is being carried out as part of the EU Network of Excellence «Complex Metallic Alloys» and COST.

¹ Hans-Rudolf Elsener, Philippe Gasser, Ulrich Klotz, Benno Zigerlig (Empa); Fazal A. Khalid (GIK, Pakistan)

Empa staff member at Tehran University

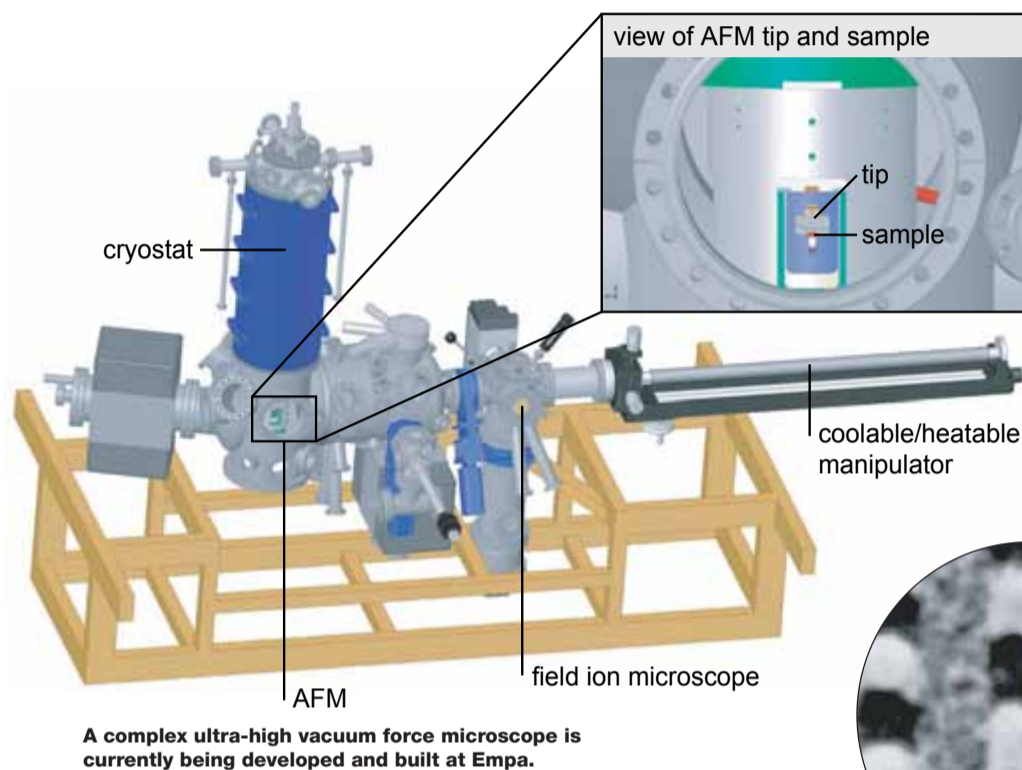
Dr Masoud Motavalli (42), Head of the Structural Engineering department at Empa, has been appointed Assistant Professor in the Department of Civil Engineering at the University of Tehran, the largest university in the Middle East. There he will be teaching undergraduate and doctoral students about «The application of polymer-composite materials in structural engineering». According to seismologists' forecasts, the risk of a severe earthquake in Tehran within the next few years is particularly high. Empa can offer a method of protection from collapsing building structure which has been tried and tested in practice: the retrospective reinforcement of masonry using high-performance fibre composite materials. Professor Motavalli is actively involved in promoting the exchange of academic knowledge in both Iran and Switzerland and regularly employs young people from abroad in his department. In order to better promote the international exchange of students, he is a founder member of the branch of IAESTE (International Association for the Exchange of Students for Technical Experience) currently being set up at the University of Tehran.



Thanks to his Iranian roots and anchorage in the Swiss structural engineering scene, Masoud Motavalli is an ideal candidate for building bridges between East and West.

Measuring forces in an ultra-high vacuum

Since its invention in 1986, the scanning force microscope has developed into an instrument that is widely used in science and industry for the imaging of surfaces. It can be used under a wide range of conditions, for example in a liquid, in an ultra-high vacuum, in magnetic fields and also at low temperatures to measure forces of very different chemical and physical natures. Dr Hans Josef Hug, professor at the University of Basel and Head of Empa's Surfaces, Coatings and Magnetism Laboratory is, together with his team of scientists, applying the latest know-how to questions in areas of fundamental research. In doing so they are finding solutions to problems encountered in, for example, data storage technology.

**MARTINA PETER**

In order to image individual bits in hard disks or domains in magnetic materials, the silicon tip of an SFM (see glossary) must be made sensitive to the magnetic leakage fields emerging from such samples. For this purpose the tip is coated with a thin ferromagnetic film only a few nanometers thick, integrated in a microfabricated cantilever, and then scanned over the surface of the sample. An SFM with a tip of this kind is known as a magnetic force microscope (MFM). Thanks to special measurement and data analysis processes developed by Hans J. Hug's research group at the Institute of Physics at Basel University (NCCR on Nanoscale Science), the lateral resolution of the MFM has been considerably improved.

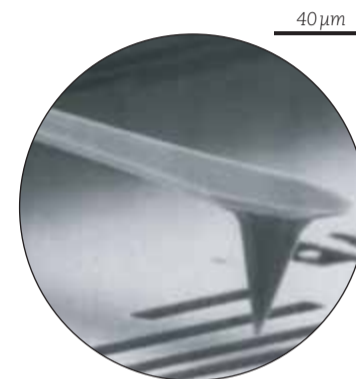
Construction of a complex ultra-high vacuum force microscope at Empa

Work is now in progress at Empa aimed at considerably improving MFM tips using the equipment for thin film production and for characterization of magnetic materials available to researchers there. It will then be possible to achieve a lateral resolution of a few nanometers. One Empa researcher is concentrating on magnetic point contacts, while others are working on reliable magnetic storage devices and magnetic shape memory alloys.

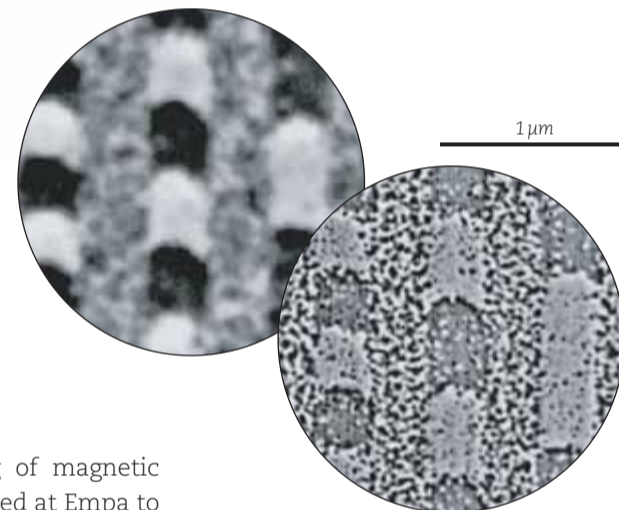
Apart from the imaging of magnetic materials, the SFM is also used at Empa to characterize surfaces on the atomic scale. The Basel Institute of Physics achieved an important breakthrough with the development of a complex force microscope (UHV-LTSFM) that operates in an ultra-high vacuum (UHV) and at low temperatures (only a few degrees above absolute zero). This was used in 2001 to measure the force between two individual atoms for the first time ever. The tip was positioned over a selected atom and then brought up close to it. The chemical link occurring between the foremost atom of the tip and the sample atom was then measured as a function of the distance between the two atoms. This provides the basis for manipulating material on an atomic scale with the SFM and combining nanostructures from individual atoms or molecules.

Physicists and mechanical engineers are currently designing and building a complex UHV-LTSFM at Empa. It will be possible to use ultra-small cantilevers (ten times smaller than those used today) in this device, thereby enabling its sensitivity to be increased by a factor of 10. This ought to make it possible, for example, not only to image individual molecules but also to observe their oscillation states and to carry out further experiments vital for basic research. ■

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The tip of an AFM integrated in a microfabricated cantilever scans the surfaces of a sample.



With the MFM (on the right) it is possible to image considerably smaller details of the bits in a hard disk compared with the devices on the market today (on left).

In 1986 the inventors of the scanning force microscope called their discovery the Atomic Force Microscope (AFM), a designation that is still common today. However, since it is possible to measure not only interatomic forces, but also forces of a different physical or chemical nature the instrument is also known today as a Scanning Force Microscope (SFM).

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- Empa internal research programmes
- NCCR Nanoscale Science (Basel University)
- SNF
- R'EQUIP
- Top Nano 21
- KTI

References:

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Structured surfaces improve fibres and textiles

The surface structure of synthetic fibres influences the properties of the textile manufactured from them. Empa has developed an embossing device that allows the surface of a single fibre to be structured in a defined way in the micrometre range.

■ RÉMY NIDERÖST

The properties of functional textiles are frequently based on the specific surface structure of the individual synthetic fibre. The fibre surface is structured on the spinning machine, but for technical reasons longitudinal structuring has only been possible up until now.

Working jointly with the Paul Scherrer Institute (PSI), Empa has now developed a simple apparatus with which the surface of synthetic fibres can also be transversely structured by embossing the structure onto the synthetic fibre. A sophisticated system ensures that the embossing effectively covers the entire fibre surface. A patent application has been filed for the principle.

The embossing system is subject to continuous further development. For example, it is not possible to connect the system directly to a fibre spinning machine since the process is still too slow. Apart from perfecting the system, another aim is to make the important step from microstructuring to nanostructuring.

Improving functionality means creating new embossing patterns. Research is therefore being carried out to establish which type of structuring produces which properties. The following areas, for example, are being investigated

– **Colour and shimmer effects:** Fashion aspects aside, these also have potential uses in safety applications.

– **Capillary action:** Important for the development of textiles designed to absorb a lot of liquid or where quick drying is desirable. The aim is to improve moisture transport by giving the fibres a special capillary structure.

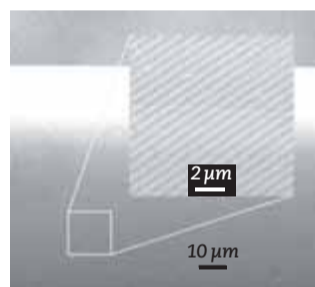
– **Friction:** Fibres with good adhesion properties, for example in fibre-reinforced concrete where the structuring of the fibres provides better anchorage in the matrix, thereby endowing the concrete with greater tensile strength.

– **Cell growth:** Certain surface structures can promote cell growth. This can be crucial for success in medical textiles.

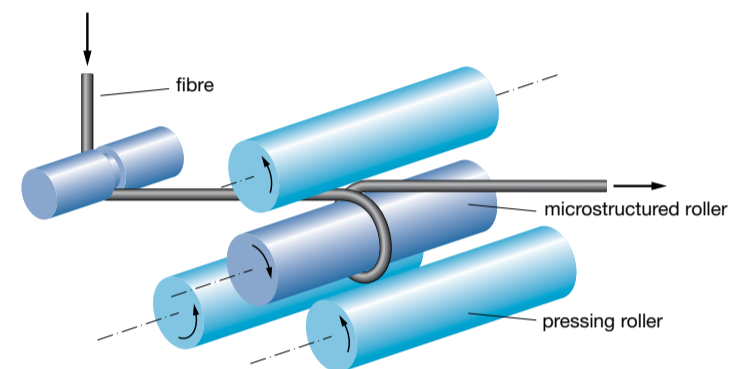
– **Lotus effect:** This is designed to produce a «self-cleaning effect».

Apart from all these functionalities, the technology could also be boosted by one of its commercial properties. Marked fibres in clothing would allow manufacturers of branded articles to make their products virtually impossible to copy or at least make them clearly distinguishable from cheap copies. ■

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Microstructured PES fibres.



Basic diagram of the microstructuring of fibres.

www.empa.ch/abt272

Spinning machine for bi-component fibres goes into service

Fibres made from two components – for increased functionality

A melt spinning machine which produces functional fibres from two thermoplastics recently went into operation at Empa. This allows the development of products with totally new, customized properties.

■ RÉMY NIDERÖST

The spinning machine for bi-component fibres «Spider» (Spinning – development – research) was commissioned at the beginning of June and produces fibres consisting of two different plastics. Bi-component fibres of this type are common today in the textile industry. The most frequently used plastics are the four thermoplastic polymers polyamide (PA), polyester (PET), polyethylene (PE) and polypropylene (PP). There are also a host of potential combinations that have yet to be explored using less common thermoplastic base materials (for example bioengineered plastics or «bioplastics»).

Special techniques such as plasma coating make it possible to construct complex fibre structures and to undertake selective chemical modifications on the fibre surface. In this way the chemical and physical properties of the fibres – for instance their hydrophilic properties, strength, shrinkage characteristics and elasticity –

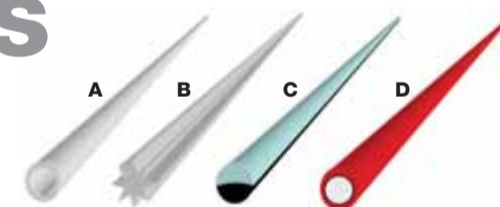
can be influenced as required. It is also possible to incorporate nanoparticles in the cladding region to achieve a desired functionality. The numerous characterization options open to Empa mean that the properties of these new fibre types can be scientifically predicted.

The object of this research is to identify fibres with specific properties for use in functional or «intelligent» textile materials for clothing, technical and medical textiles or fibre composites. Possible functions of these innovative textiles include the controlled release of drugs in medical plasters, shock absorbers in protective clothing, temperature control in firemen's suits or sportswear and applications in sensor technology (for instance changing colour to indicate environmental changes). Materials can thus be tailored to make them biocompatible, biologically degradable, moisture-repellent or extra absorbent, flame-retardant or odour-reducing as required.

One particularly promising avenue is to manufacture fibres with photovoltaic or thermoelectric properties. These could convert the energy of light or the body temperature into electric current – turning a suit into a power plant!

«Spider» is used by Empa not only for its own research programmes, but also for joint projects with partners from industry and science. An interesting aspect of the system is its size. While pure research uses just a few grams of plastic, industrial-scale operations involve many thousands of tonnes. The research system installed at Empa's St. Gallen facility, however, is designed for quantities of a few kilograms. This produces results that can be reliably extrapolated up to an industrial scale while still only using a small amount of material. ■

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Fibre types:
A Hollow fibre
B Star-shaped section fibre
C Side-by-side bi-component fibre
D bi-component fibre with core/cladding structure.



Multifilament spinneret. The liquid polymer is forced through the spinning nozzles at temperatures up to 300°C and a pressure of up to 100 bar. In this way a large number of bi-component fibres can be spun and processed simultaneously.

www.empa.ch/abt272

Dwarfs with undefined risks

Nanotechnology is expected to open the way for materials with new functionality, for tailored drugs, for even faster computers and far more besides. On 29 June the Empa Academy provided a discussion platform for debating the subject of «Nanotechnology: Opportunities and Risks».

■ SABINE OLFF

If you reduce a material to nanometre-sized particles (a nanometre is a millionth of a millimetre), you can completely change its properties. The advance into the nano cosmos will provide the key to nature's blueprints. This opens the way to the development of scratch-proof paints, self-cleaning windows or tailored drugs, to mention just a few examples.

Nanotechnology affects us all

«In the long-term there will be no sector of the economy left untouched by nanotechnology», prophesies Dr Annabelle Hett who heads a network at SwissRe for the early identification of risk factors. The opportunities of the new technology are enormous. However, she stresses that «we have to consider benefits and risks alike». This is a task for science, industry, government and society.

There was unanimous agreement on the benefits of nanotechnology at the 18th Science Apéro at the Empa Academy. On the other hand there were conflicting views on how the risks should be assessed. «There are plausible scenarios indicating that certain risks are to be expected», said the philosopher and ethicist Dr. Klaus Peter Rippe.

Nanoparticles are tiny and extremely mobile. If they are not firmly embedded in a solid (for example as in the Teflon coating of frying pans) or liquid (as in paints), they could be inhaled and pass into the bloodstream. Whether the particles can also diffuse through the skin is currently under investigation. What processes the particles might possibly set in motion and whether they are harmful to the health are unknown factors. The example of the Degussa company which has been manufacturing nanopowders for about 30 years shows that the health of employees has apparently not been harmed through exposure. However, information about whether nanotechnology is dangerous will only be forthcoming in the future as a result of numerous exposure studies based on animal

The panel of experts (from l. to r.):
Dr Annabelle Hett (SwissRe), Hans Näf (Bühler AG),
Prof. Dr Louis Schlapbach (Empa),
Dr Klaus Peter Rippe (ethik im diskurs)



The discussion on the opportunities and risks of nanotechnology drew a large audience to the Empa Academy.

experiments, toxicological studies and long term experience. That needs time and a certain residual risk will always remain.

Eliminating risks

The question is how to deal with the present uncertainty. For the ethicist Klaus Peter Rippe the precautionary principle applies. This means that nano technicians in science and industry should think about possible dangers and eliminate the risks. Another question is the present situation with regard to the protection of employees working at companies that produce nanoparticles. «We follow the rules and regulations of the Institute for New Materials (INM) in Saarbrücken, which, for instance, cover working in the fluid phase», said Hans Näf from Bühler AG. The company recently started manufacturing scratch-proof paints by adding nanoparticles.

According to Prof. Louis Schlapbach, the Federal Office for Professional Education and Technology has asked Empa to help with risk analyses in the biology area. There are also a number of projects at EU level. Klaus Peter Rippe warned, however, against waiting for the government to come up with legislation: «It took twelve years until the law on genetic engineering was legally valid.» He called instead for networked initiatives by science and industry – ideally at international level. According to Annabelle Hett initiatives of this type were already in progress: «Large companies are currently forming consortia in which they are attempting to analyze the risks and to develop risk management systems.» Such early intervention with a new technology is unique in history.

However, as one attendee commented, it was necessary to empathise with the emotions expressed by the public. The use of technical arguments in response to their fears was the wrong way to go about it. Annabelle Hett agreed: «If society does not support nanotechnology because it is afraid of it, we will miss lots of opportunities.» (Vs) ■

Exploiting discoveries in nano- and microtechnology

The personal initiative of four men from the business, educational and research scene in St. Gallen and Buchs led to the founding of the non-profit making «Association for the Promotion of Nano/Microtechnology in the Lake Constance Region». One of the founding fathers is Xaver Edelmann, a member of the governing body of Empa. For this reason the Association is also based at Empa in St. Gallen.

The purpose of the Association is to encourage the implementation of research results in the field of nano and microtechnology as a means of boosting the innovative strength and competitiveness of companies. It aims to preserve or create jobs with application-oriented projects and with inter-company joint ventures and cooperation at national level. Contracts have already been concluded with the State Secretariat for Economic Affairs (seco) and the canton of St. Gallen, which have together pledged 2.3 million francs up to 2007. The Association itself has to contribute 865,000 francs. One of the first major projects is to support the Nanofair and Nano-conference in September 2004 and the micro and nanotechnology master course (MNT).

Empa Summer Camp for Kids

From 12 to 16 July 2004 18 children of Empa staff members had the opportunity to explore the world of research and technology at first hand. Under professional supervision, the seven-to-thirteen year olds spent part of their summer holidays looking around eight different departments at Empa. They eavesdropped on a world of sound, and discovered that the air and rain are not always clean. They learned to think of wood in a new light, as a natural building material which hides many secrets. They experienced an indoor cloudburst, an ice-age in midsummer and silk-screened their own T-shirts. The aim of the summer camp is to help parents to better harmonize the needs of family and profession, but it is also hoped that it will arouse the children's interest in scientific and engineering professions.



Fun, family-friendly holiday supervision and a chance to learn what science is all about.

From the press

Press gleanings

Neue Zürcher Zeitung

Item in the NZZ newspaper, 2 July 2004, «Swiss researchers shoring up EU railway bridges».

Empa and EPF Lausanne (EPFL) are taking part in an EU project aimed at guaranteeing the safety of railway bridges. Empa is taking a leading role in electronic monitoring while EPFL is studying the effects of fatigue on the safety of steel-reinforced concrete bridges. (SDA)

Opinion

“ Working with nanotechnology demands imagination from scientists so that they can foresee possible risks at an early stage. What is dangerous is to assume that this technology can already be regarded as risk-free. ”



Dr Klaus Peter Rippe
Director «ethik im diskurs»
Philosopher and ethicist
President of the Swiss Ethics
Committee for Gene Technology

Impressum

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