

MaP Graduate Symposium

featuring the MaP Award 2016

The 11th Annual Gathering of Materials & Processes Researchers at ETH Zürich

Thursday, 9 June 2016

ETH Zürich, HG E5 and E-floor main hall

Rämistrasse 101, 8092 Zürich

Symposium Booklet

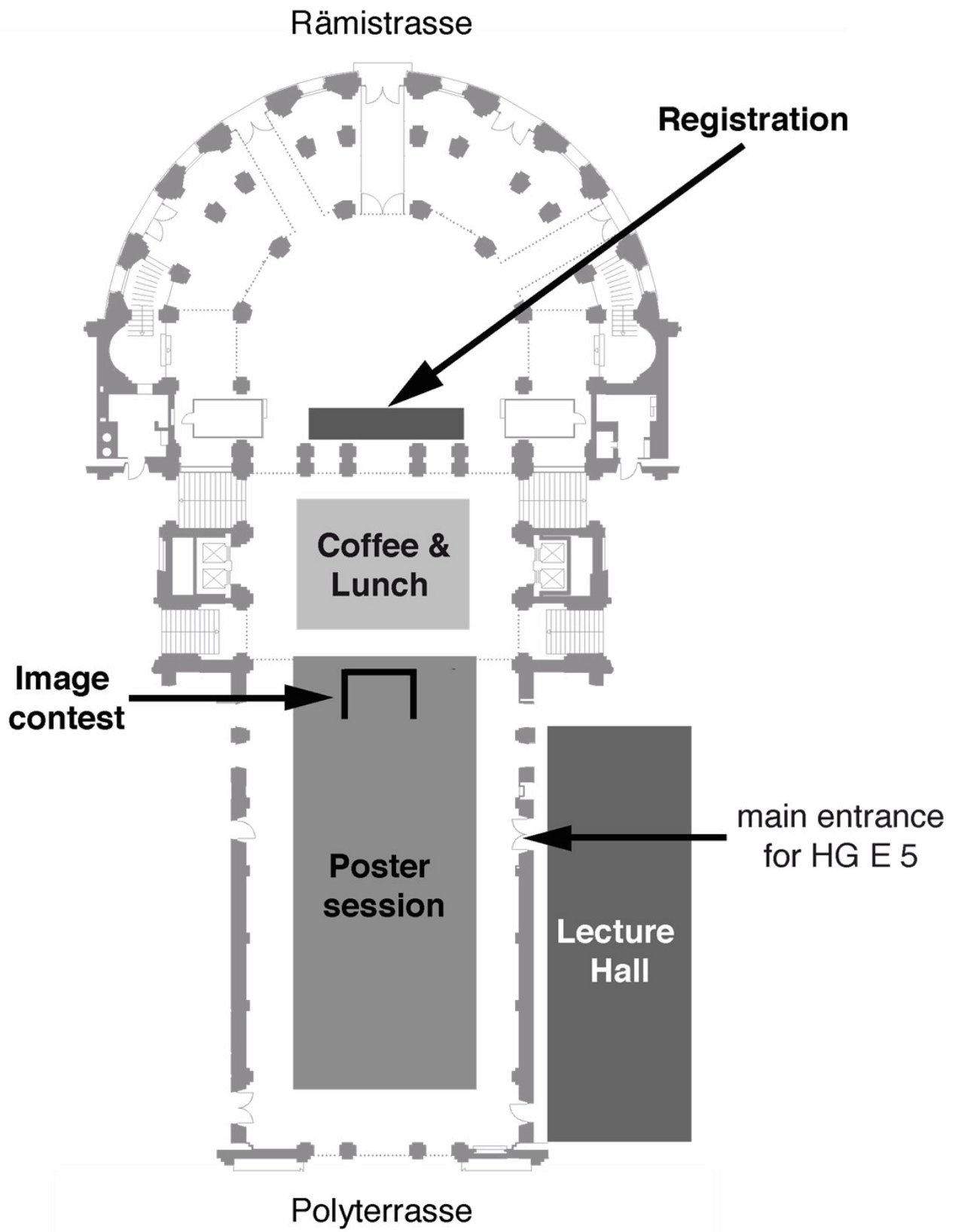
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PROGRAM

08.00	<i>Registration</i>
08.50	Prof. André R. Studart, MaP Director Opening remarks
09.00	Mario Stucki, Functional Materials Laboratory, D-CHAB Surface Coated Template Particles for Internally Functionalized Pores in Water-proof and Breathable Membranes
09.15	Vincenzo Costanza, Mechanics & Materials, D-MAVT High Sensitivity Bionic Hydrogels for Temperature-Mapping Skins
09.30	Hen-Wei Huang, Multi-Scale Robotics, D-MAVT Biomimetic Soft Micromachines with Programmable Morphology and Motility
09.45	Martina Pepicelli, Soft Materials, D-MATL Semiflexible Microtensiometers for Accurate and Local Langmuir Monolayer Characterization
10.00	Michael Kant, Transport Processes & Reactions, D-MAVT Spallation Drilling – A Novel Drilling Technology with the Potential to Boost Deep Geothermal Energy in Switzerland
10.15	<i>Coffee Break & Poster Session</i>
11.00	Tobias Keplinger, Wood Materials Science, D-BAUG Strategies for the Development of Smart Wood-Based Materials
11.15	Athena Economides, Computational Science & Engineering Laboratory, D-MAVT Simulation of Microfluidics Devices for Mechanical Cell Separation
11.30	Flora Chiu, Biochemical Engineering, D-CHAB Microfluidic-Based Droplet and Cell Manipulations Using Swimming Artificial Bacterial Flagella
11.45	Hortense Le Ferrand, Complex Materials, D-MATL Using Magnetic Fields to Design and Build Functional Graphene-Based Composites
12.00	<i>Lunch & Poster Session</i>

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13.30	Dr. Ivo Leibacher , <i>Mechanics & Experimental Dynamics, D-MAVT</i> Acoustophoresis of Cells, Core-Shell Particles, Disks and Droplets
13.50	Dr. Arabella Mauri , <i>Experimental Continuum Mechanics, D-MAVT</i> Multiscale Mechanical Behavior of Fetal Membranes
14.10	Dr. Christian Peters , <i>Micro & Nanosystems, D-MAVT</i> Biodegradable Superparamagnetic Polymer Composites: From Material Identification to Device Application
14.30	Dr. Gianvito Vilé , <i>Advanced Catalysis Engineering, D-CHAB</i> Design of New Nanostructured Catalysts for Selective Hydrogenations in Flow
14.50	<i>Coffee Break</i>
15.30	Ye Tao , <i>Spin Physics & Imaging, D-PHYS</i> Single-Crystalline Ferromagnetic Nanowires with Completely Controlled Crystal Orientation
15.45	Songbo Ni , <i>Interfaces, Soft Matter & Assembly, D-MATL</i> Programmable Assembly of Hybrid Colloidal Molecules
16.00	Vijay Jain , <i>Photonics Laboratory, D-ITET</i> Optical Control of a Vacuum Levitated Nanoparticle
16.15	Magdalini Panagiotakopoulou , <i>Thermodynamics in Emerging Technologies, D-MAVT</i> Paramorphotic Youth: A 3D Nanoprinted Model Unveils a New Mechanism of Cancer Cell Migration
16.35	Flash Poster Presentations
16.45	Industry Presentations
17.15	Award Ceremony
17.45	<i>Industry Apéro Riche</i>

ABSTRACTS OF TALKS

Session 1: 09.00 – 10.15

Surface Coated Template Particles for Internally Functionalized Pores in Waterproof and Breathable Membranes

Mario Stucki, Christoph R. Kellenberger, and Wendelin Stark

Functional Materials Laboratory, D-CHAB, ETH Zurich

In recent years the public attention towards chemicals released to the environment has increased. In 2013, upon the discovery of multiple potentially dangerous and persistent chemicals in outdoor apparel^[1], the global NGO Greenpeace initiated the campaign “Detox” to convince global outdoor brands to switch to alternative materials. Replacements were only partially given at the time, *i.e.* a completely porous, functional membrane was not amongst them. With the template removal method, shown in 2012^[2], the optimal tool to find a new, environmentally benign way to produce fully porous, waterproof and breathable membranes, was available.

Commercial soft polyurethane was dissolved and mixed with template particles through ball milling. The resulting dispersion was spread on a flat surface and dried. Upon template removal a porous structure was obtained. With untreated template particles the requirements of the outdoor industry could not be met and additional practical problems like shrinking or collapsing of the porous network was observed. To overcome this, the template particles were coated with a single layer of stearic acid to increase hydrophobicity^[3]. Using a high particles to polymer ratio (4:1 in weight) a sufficiently porous network was created to allow complete template removal, which is not obvious regarding the use of fillers in many polymers. The significant increase in water proofing (300%) showed the hydrophobic nature of the internally coated porous network. Surprisingly, the apparent diameter of the pores repelling water did not affect the diffusive pathway of water vapor, therewith breathability was kept at a constant high level. Furthermore, less pore deformation was observed upon template removal. To prove the large scale feasibility, 5.8 m² of membrane were produced and laminated to a Nylon fabric. The final laminate was tailored into a functional rain jacket prototype.

[1] M. Santen and U. Kallee, Greenpeace (2012); [2] C. R. Kellenberger et al., WO2012097967 (A1) (2012); [3] M. Stucki and W. J. Stark, EP15198440.8 (2015)

High Sensitivity Bionic Hydrogels for Temperature-Mapping Skins

Vincenzo Costanza¹, Raffaele Di Giacomo¹, Luca Bonanomi¹, Bruno Maresca^{1,2}, and Chiara Daraio^{1,3}

¹ *Mechanics & Materials, D-MAVT, ETH Zurich*, ² *Università di Salerno (Italy)*, ³ *Aeronautics & Applied Physics, California Institute of Technology (USA)*

Synthetic skins¹ are essential to augment robotics² and improve prosthetic limbs³. Existing platforms are designed to emulate properties of the human skin, by incorporating artificial sensing functions³⁻⁷. Among them, response to temperature variations has been demonstrated^{3, 7}, albeit with poor sensitivity. Human skin senses temperature with high sensitivity, exploiting a set of voltage-gated ionic-channel transmembrane proteins⁸, which are distributed with different spatial densities in different areas of the body⁹. Here, we describe a biological, pectin hydrogel with extremely high temperature sensitivity. We fabricate transparent, self-standing, flexible films, which are able to detect minute temperature variations. We realize skins that map temperature with different spatial resolutions. These materials are ultra-low cost and biocompatible. They can be used as sensitive layers to monitor heat transfer on surfaces or integrated into large area skin platforms.

[1] J.-Y. Sun et al., *Adv. Mater.* **26**, 7608 (2014); [2] M. Kaltenbrunner et al., *Nature* **499**, 458 (2013); [3] J. Kim et al., *Nature Commun.* **5**, 5747 (2014); [4] B. C.-K. Tee et al., *Nature Nanotech.* **7**, 825 (2012); [5] B. Nie et al., *Adv. Mater.* doi:10.1002/adma.201502556; [6] C.-K. Benjamin et al., *Science* **350**, 313 (2015); [7] M. Segev-Bar et al.,

Biomimetic Soft Micromachines with Programmable Morphology and Motility

Hen-Wei Huang¹, Mahmut Selman Sakar², and Bradley Nelson¹

¹ Multi-Scale Robotics, D-MAVT, ETH Zurich, ² Institute of Mechanical Engineering, EPFL

Nature provides a wide range of inspiration for building mobile micromachines that can navigate through confined heterogenous environments and perform minimally invasive environmental and biomedical operations. For example, microstructures fabricated in the form of bacterial or eukaryotic flagella can act as artificial microswimmers. Due to limitations in their design and material properties, these simple machines lack multifunctionality, effective addressability, and maneuverability in complex environments. Here, we develop an origami-inspired rapid prototyping process for building self-folding, magnetically powered micromachines with complex body plans, reconfigurable shape, and controllable motility. The swimming characteristics of these micromachines can be dynamically modulated by selective reprogramming of their mechanical design and magnetic anisotropy. We find that tail and body morphologies together determine swimming efficiency and, unlike for rigid swimmers, the choice of magnetic field can subtly change the motility of these soft micromachines.

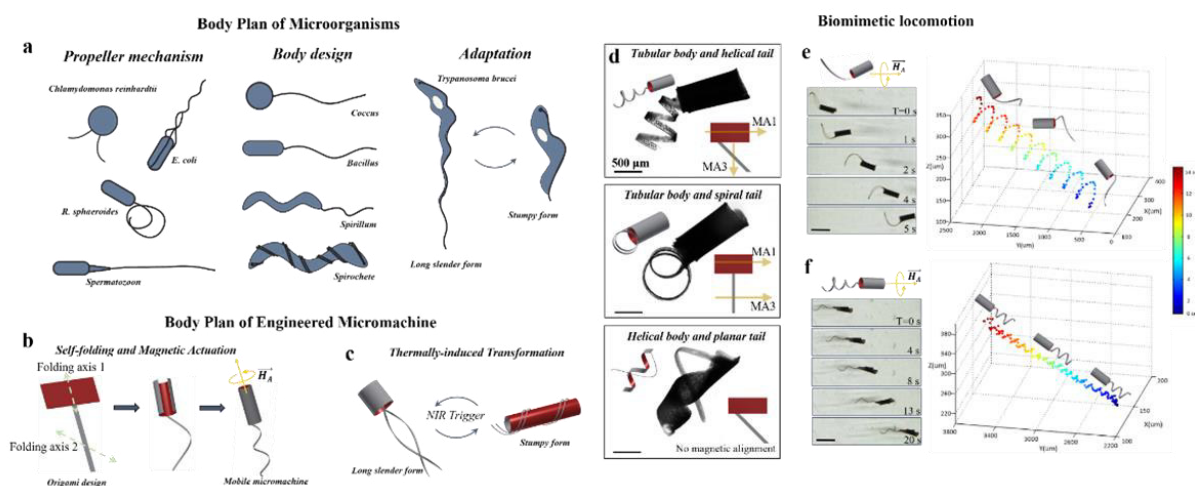


Fig. (a) The body plan of microorganisms is composed of the propeller mechanism, body design and shape adaptation. Shape contributes a measure of survival value in the face of nutrient acquisition, cell division, predator and motility. (b) The body plan of engineered mobile micromachines is programmed in self-folding bilayer structures. (c) The shape shifting of micromachines could be triggered by applying near-infrared light. (d) The optical images of the fabricated soft micromachines with different body plan. (e) and (f) The locomotion trajectories of the soft micromachines with identical tubular body attaching with planar tail and helical tail respectively. The machine with planar tail performing undulatory motion swims 3 times faster than the machine with helical tail performing corkscrew like motion.

Semiflexible Microtensiometers for Accurate and Local Langmuir Monolayer Characterization

Martina Pepicelli¹, Pieter Gijsenbergh², Chris L. Wirth³, Robert Puers², and Jan Vermant¹

¹ Soft Materials, D-MATL, ETH Zurich, ² KU Leuven ESAT-MICAS Leuven (Belgium), ³ Chemical & Biomedical Engineering Department, Cleveland State University (USA)

One of the most interesting aspects in the vast world of interfacial science regards the development of new challenging techniques to probe and measure rheological properties of complex fluid-fluid interfaces.

Standardly, in interfacial science, surface pressure-area isotherms are measured using a platinum plate connected to a Wilhelmy balance. Nevertheless, this widely used technique has numerous disadvantages: evaporation and buoyancy effects, distortion of the interfacial stress profile around the probe and limited frequency range of oscillatory rheological measurements. With the goal of overcoming these restraints and at the same

time increasing the sensitivity of the technique, a miniaturized setup for tensiometry measurements has been developed and tested, based on an earlier idea by Zell et al. [1,2].

This set-up consists of a microtensiometer made out of a semi-flexible polymer structure placed at the interface. The gradient in surface pressure between the in- and outside of the tensiometer will cause the device to be compressed through flexible millimeter-scale springs. Using an optical set-up, the tensiometer deflection and hence the related surface pressure can be determined. Proof-of-principle oscillatory measurements showed a remarkable agreement between the values of surface pressure independently detected by the Wilhelmy balance and by the tensiometer.

Furthermore the instantaneous response of the tensiometer setup allows for high frequency measurements, up to frequencies in a range much higher than currently reported in the literatures [2].

[1] P. Gijsenbergh et al., *Sensors and Actuators A* **229**, 110 (2015); [2] Z.A. Zell et al., *Appl. Phys. Lett.* **97**, 133505 (2010)

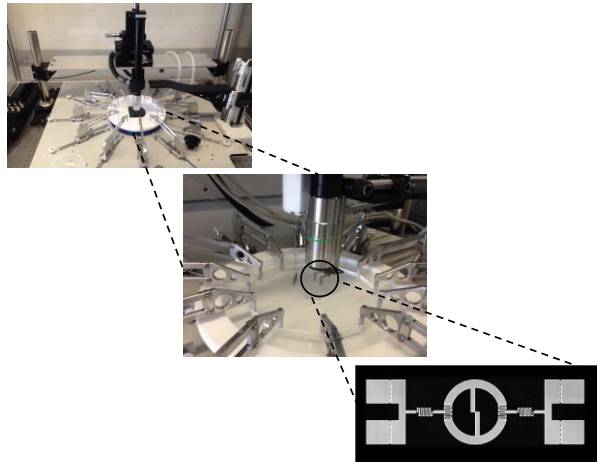


Fig. Radial trough apparatus equipped with an optical train system to visualize the microtensiometer for surface pressure measurements.

Spallation Drilling – A Novel Drilling Technology with the Potential to Boost Deep Geothermal Energy in Switzerland

Michael Kant¹, Claudio Madonna², and Philipp Rudolf von Rohr¹

¹ Transport Processes & Reactions, D-MAVT, ETH Zurich, ² Geological Institute, D-ERDW, ETH Zurich

In order to promote the development of geothermal energy production from deep resources, cost effective processes to increase the drilling performance in hard rocks have to be developed. To this end, different novel technologies are currently investigated by researchers around the world. Among the different attempts to intensify the conventional drilling process, spallation drilling is a promising approach. This process is based on the effect of hard, crystalline rocks disintegrating into small fragments, when rapidly heated by a hot fluid jet. Previous research has indicated that spallation drilling could decrease the drilling costs due to higher drilling velocities and significantly reduced tripping and maintenance time.



At the Institute of Process Engineering (ETH Zurich) various spallation drilling experiments from small rock probes to large-scale granite blocks have been successfully performed in different experimental facilities. These experiments have proven the feasibility of spallation drilling as a standalone technology and in combination with mechanical drilling. The operating range where the spallation process can be successfully initiated was investigated and the required flame properties have been defined. Additionally, the influence of the rock formation, the confinement pressure and the rock properties on the process was evaluated. The research has been performed in close cooperation with the Geological Institute of ETH Zurich, in order to develop appropriate models describing the spallation process and therewith enhancing the required knowledge about this technology. From the experimental tests conclusions on the feasibility, benefits and limitations of such a technology can be drawn. As a next step, field tests will be performed to further develop the process and to prove the operational readiness of this technology.

Session 2: 11.00 – 12.00

Strategies for the Development of Smart Wood-Based Materials

Tobias Keplinger^{1,2}, Etienne Cabane^{1,2}, and Ingo Burgert^{1,2}

¹ Wood Materials Science, D-BAUG, ETH Zurich, ² Applied Wood Materials Laboratory, Empa

One of the main challenges of the 21st century is the transformation of our current society towards sustainability and wood as an abundant, CO₂ storing resource has the potential to become one of the key materials. Wood has been used for thousands of years as an engineering material due to its properties including aesthetic appearance, easy availability and exceptional mechanical properties compared to its lightweight.

In recent years novel functionalization techniques, either be used to improve the wood intrinsic properties (low dimensional stability and durability), or for the development of advanced wood based hybrid materials, have been developed. By using wood as a natural scaffold one can directly profit from the hierarchical structure of wood across several length scales. This helps to circumvent the common difficulties in materials science of the upscaling process of complex hierarchical structures in bottom up approaches.

In this regard different strategies for the design of wood-based polymer hybrid materials, which retain the structural integrity of wood, for novel applications in order to better utilize the renewable resource are presented. A spatially controlled and selective modification can be achieved, by different modular polymerization grafting techniques (including FRP and ATRP) within the macromolecular assembly of the secondary cell walls. These techniques not only allow to hydrophobize specific regions of the cell wall but also to incorporate pH-dependent water uptake by the incorporation of polyelectrolytes. Additionally new composites were achieved via a pore filling technique, where temperature responsive PNIPAM hydrogels were in-situ formed within the wood lumina [1-4]. We believe that these presented functionalization approaches help to promote the utilization of wood in new application fields and emphasize the potential of wood in materials science.

[1] T. Keplinger et al., *Acta Biomaterialia* **11**, 256 (2015); [2] T. Keplinger et al., *Advanced Materials Interfaces* **accepted**; [3] E. Cabane et al., *ChemSusChem* **7**, 1020 (2014); [4] E. Cabane et al., *Scientific Reports* **in review**

Simulation of Microfluidics Devices for Mechanical Cell Separation

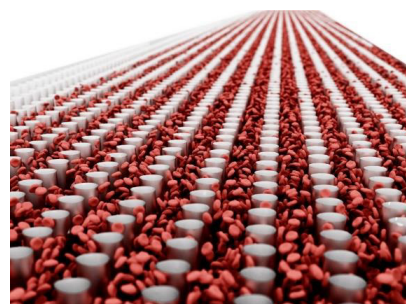
Athena Economides, Sergey Litvinov, Dmitry Alexeev, Christian Conti, Diego Rossinelli, and Petros Koumoutsakos
Computational Science & Engineering Laboratory, D-MAVT, ETH Zurich

Advances in medicine and pharmaceutical research have led to the creation of devices capable of handling fluids and biological matter in the microscale. Here, we focus on microfluidic systems, for the mechanical detection and separation of Circulating Tumor Cells (CTCs) from the blood stream, as well as clusters of CTCs, to serve as indicators of metastatic cancer.

Our simulations are based on an extension of Dissipative Particle Dynamics (DPD). DPD is a mesoscale simulation technique that has been shown to accurately resolve solid-fluid-cell interactions with sub-micron resolution. We use uDeviceX, an open-source high-throughput in-house developed software with kernels thoroughly optimized for GPUs, for microfluidics simulations using state-of-the-art DPD models.

Through these predictive simulations we seek to elucidate and characterize the fundamental processes governing the flow of blood, CTCs and other cells in confined geometries and assist the design of microfluidic devices for the effective isolation of CTC clusters and bacteria in blood samples. Detailed understanding of flows at the microscale will enable technology advancements in the microfluidics chip design for future technologies.

[1] D. Rossinelli et al., *Proceedings of the International Conference for High Performance Computing, Networking, Storage and Analysis*. ACM, (2015)



Microfluidic-Based Droplet and Cell Manipulations Using Swimming Artificial Bacterial Flagella

Yun Ding¹, Famin Qiu², Flora W. Y. Chiu¹, Bradley J. Nelson², and Andrew J. deMello¹

¹ Biochemical Engineering, D-CHAB, ETH Zurich, ² Multi-Scale Robotics, D-MAVT, ETH Zurich

Magnetically controlled artificial bacterial flagella (ABFs) are recognized as a highly promising micro-robotic tool for biomedical applications, including minimally invasive surgery and targeted drug delivery. ABFs are inspired by flagellated bacteria, where thin, whip like appendages protruding from the cell body are used to move the bacteria towards chemo-attract-

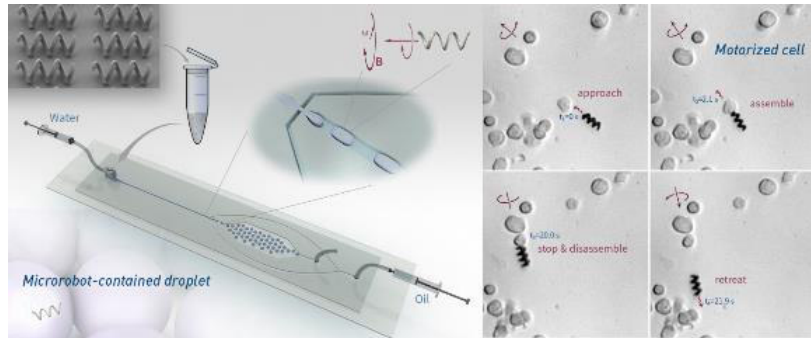


Fig. The process of encapsulating ABFs in droplets (left) and an example of cell manipulation (right).

ants. ABFs have been used to address the challenging issue of swimming within low Reynolds number regimes typical on the microscale. In recent years, research has explored and characterized their abilities in both *in vitro* and *in vivo* scenarios. In the current work, the manipulation of soft particles (including droplets and single cells) using ABFs is investigated and validated for the first time. Significantly, precise and controlled ABF locomotion is demonstrated within confined fluid volumes (such as water-in-oil droplets). Over the past decade, the controlled and high-throughput delivery of specific components (such as cells, organic molecules and reagents) into microfluidic droplets has emerged as a powerful and unique tool for processing biological and chemical experiments in an efficient and massively parallel manner. Herein, we show that ABFs offer new opportunities for manipulating and transporting species inside such droplets. This includes demonstration of the intimate interaction between ABFs and both microdroplets and Human B lymphocyte cells. Such methods allow the controlled assembly/disassembly of objects with complex configurations. We recognize that droplet/cell-ABF assemblies could be used to mimic microorganisms, while "motorized" B cells have the potential to enable targeted immunotherapies *in vivo*. We believe that ABFs represent an exciting and unique engineering tool for droplet- and cell-based experimentation.

Using Magnetic Fields to Design and Build Functional Graphene-Based Composites

Hortense Le Ferrand¹, Sreenath Bolisetty², Ahmet F. Demirörs¹, Rafael Libanori¹, André R. Studart¹, and Raffaele Mezzenga²

¹ Complex Materials, D-MATL, ETH Zurich, ² Food and Soft Materials, D-HEST, ETH Zurich

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13.30 – 14.50



Acoustophoresis of Cells, Core-Shell Particles, Disks and Droplets

Ivo Leibacher

Mechanics & Experimental Dynamics, D-MAVT, ETH Zurich

Acoustophoresis means the movement of particles and objects in a fluid by acoustic radiation forces, which are generated by acoustic waves. The technology is also referred to as "ultrasonic particle manipulation". It has numerous applications for the contactless handling of various particles and objects, mainly in the field of micro-technology.

Acoustophoresis has manifold applications e. g. for biological cells. In the life sciences, acoustophoresis allows operations for the realization of a "lab-on-a-chip", which means the miniaturization of biochemical processes on fast and cheap microsystems. As outlined in this thesis, there is broad application potential also for the acoustic handling of fluid droplets, disk-shaped particles and core-shell particles.

In this dissertation, acoustophoresis was examined in microfluidic acoustic domains in the size range of micrometers to centimeters with ultrasonic frequencies in the kilohertz to megahertz range. The particle sizes ranged from 5 μm to 500 μm . Microfluidic structures were fabricated in silicon by microtechnological, wafer-based fabrication methods. In the silicon, fluid cavities were fabricated to introduce suspended particles for subsequent manipulation by piezoelectric acoustic excitation.

More specific, three main topics are discussed: First the acoustophoresis of particles with various shapes has been examined. Acoustophoresis of hollow particles and droplets was demonstrated as well as acoustophoretic rotation of non-spherical particles such as disks. Secondly, applications of acoustophoresis, such as cell focusing in a single-cell printer or particle sorting, were demonstrated. Thirdly, two-dimensional acoustophoretic fields were generated, which allows novel acoustophoretic manipulations beyond the possibilities of the common one-dimensional fields.



Multiscale Mechanical Behavior of Fetal Membranes

Arabella Mauri

Experimental Continuum Mechanics, D-MAVT, ETH Zurich

The fetal membrane is a thin and strong membrane, which surrounds the fetus during the entire gestation period to protect and preserve its environment. In 1% to 2% of all pregnancies, the membrane suddenly ruptures prior to the 37th week of gestation and without contractions, resulting in a preterm birth with high risks of morbidity and mortality for the newborn. Mechanisms leading to the timely rupture of the membrane have not yet been completely understood and are linked to the local deformation and rupture behavior of the membrane. This thesis focuses on the mechanical characterization of the fetal membrane at different length scales and on the formulation of corresponding models to investigate clinically relevant loading conditions.

A comprehensive set of experimental investigations at macroscopic (1-10 mm) and microscopic (10-100 μm) length scales was generated using novel experimental setups and protocols. The collagen microstructure of fresh, hydrated and unfixed membranes was visualized through second harmonic generation and multiphoton microscopy. These techniques enable the three-dimensional visualization during mechanical tests of the spatial and hierarchical arrangement of collagen fibers and of the position of cell nuclei. Relevant microstructural parameters such as thickness, collagen orientation and distribution were quantified from microscopy images for different loading conditions and helped rationalizing the structural response of the material.

Two fundamentally different modeling approaches – a continuum model and a discrete network model – were proposed to rationalize the complex deformation behavior of the human amnion and were validated with the experimental data based on both the macroscopic and microscopic deformation behavior.



Biodegradable Superparamagnetic Polymer Composites: From Material Identification to Device Application

Christian Peters

Micro & Nanosystems, D-MAVT, ETH Zurich

The human body is transparent to magnetic radiation and the interaction of magnetic fields with biological tissue is non-problematic. These circumstances promote untethered magnetic microdevices as promising tools and building blocks for many biomedical applications *in vivo* and *in vitro*. While the largest portion of research focuses on the development of novel devices and applications, fundamental questions regarding localization and

recovery of these devices after their *in vivo* use remain largely overlooked. However, the device fate inside the human body may lead to severe medical implications with potentially lethal outcome and device recovery must be considered. To provide a comprehensive solution that addresses device application and fate at the same time, this work demonstrates degradable, superparamagnetic nanocomposites as a one-step solution for device fabrication, actuation and application, while rendering post-application device recovery unnecessary. The Artificial Bacterial Flagella, a bio-inspired helical swimming microrobot, is selected to demonstrate the feasibility of this proposal. As degradable magnetic composite microdevices have not been proposed to date, a bottom-up approach is selected in which appropriate composite materials, fabrication schemes, and actuation principles are identified and developed in accordance with each other, and subsequently combined to demonstrate device application and biocompatible degradation. The results presented throughout this work manifest the feasibility of degradable superparamagnetic composite materials in general, and ABFs in particular, for next generation biomedical applications *in vivo*.



Design of New Nanostructured Catalysts for Selective Hydrogenations in Flow

Gianvito Vilé

Advanced Catalysis Engineering, D-CHAB, ETH Zurich

Hydrogenation reactions have relied for decades on the use of catalysts containing high-loading precious metals (e.g., Pd, Pt) and toxic poisons (e.g., Pb). This research originates from the need to replace these existing systems, nowadays posing environmental and economic concerns due to the presence of noxious elements and for the poor metal utilization. In this context, the alkyne and nitroarene hydrogenations have been targeted as two industrially-relevant case studies. These transformations, in fact, are widely applied for manufacturing building blocks for polymers, agrochemicals, fragrances, and pharmaceuticals. New families of materials were discovered and rationalized: metal oxides, ligand-modified metal nanoparticles, and single-atom metal centers. With respect to gas-phase processes, the established concept that oxides cannot selectively catalyze the reaction due to a limited H₂-splitting ability has been discarded, ascertaining the outstanding performance of ceria in acetylene and propyne hydrogenation. Density Functional Theory calculations, spectroscopic analyses, and tailored synthetic methods have shed light on the structure-redox-performance relationships of the material. Besides, it has been shown that the activity can be further enhanced by doping this intriguing oxide with trivalent cations, such as gallium and indium. For liquid-phase processes, the first ligand-modified nanocatalysts reaching industrial scale have been rationalized. The materials contain ten-fold less metal and are modified with a water-soluble ligand. This ligand not only isolates the metal but also contribute to catalysis, in the H₂-splitting. Finally, the work has uncovered the precision synthesis, characterization, evaluation, and molecular-level understanding of the first single-site catalysts obtained by stabilizing metal atoms in cavity-like structures. This demonstrates that the classical strategy of poisoning the metal (with lead) to reduce the ensemble where the reaction takes place can be brought to a new dimension at the atomic scale.

Session 3: 15.30 – 16.30

Single-Crystalline Ferromagnetic Nanowires with Completely Controlled Crystal Orientation

Ye Tao and Christian Degen

Spin Physics & Imaging, D-PHYS, ETH Zurich

Programmable Assembly of Hybrid Colloidal Molecules

Songbo Ni^{1,2}, Jessica Leemann^{1,2}, Ivo Buttinoni¹, Lucio Isa¹, and Heiko Wolf²

¹ Interfaces, Soft Matter & Assembly, D-MATL, ETH Zurich, ² IBM Research Zurich

Patchy colloids have drawn a tremendous attention over past years, due to their great potential in constructing colloidal superstructures as well as in fabricating active colloids. Despite the remarkable progress in fabrication of patchy particles, current methods are commonly limited to simple compositions and geometries. Here, we present a novel method based on sequential capillary assembly on topographical templates, which achieves unprecedented control over the composition and geometry (Fig. a and b)¹. With our technique more than two species can be integrated deterministically in different geometries (Fig. 1c). The composition of such colloidal molecules is defined by the filling sequence of different particles, while the shape of the assembly sites (traps) on the template determines their geometry independently. The assembled colloidal molecules can be further mechanically linked, harvested and dispersed in solution for various applications. These fully programmable colloidal molecules open up new directions, not only to assemble and study complex materials with single-particle-level control, but also to fabricate new microscale devices for sensing, patterning and delivery applications.

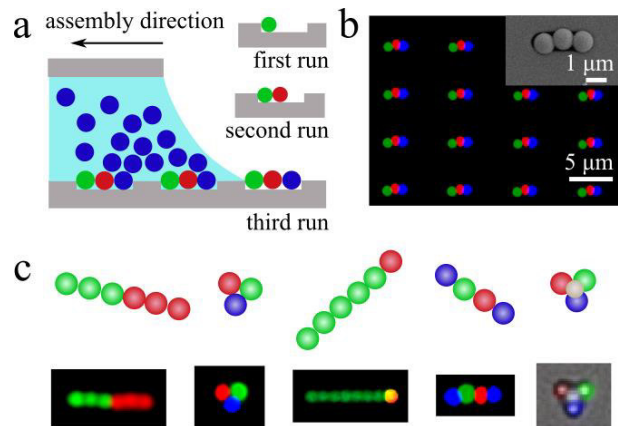


Fig. (a) Schematic representation of sequential capillary assembly for linear molecules. (b) Merged fluorescence image of colloidal chains composed of green, red and blue polystyrene particles. Inset: the SEM of a colloidal chain in the template. (c) Library of various colloidal molecules (merged fluorescence images).

[1] S. Ni et al., *Sci. Adv.* **2**, e1501779 (2016)

Optical Control of a Vacuum Levitated Nanoparticle

Vijay Jain^{1,2}, Jan Gieseler¹, Clemens Moritz³, Christoph Dellago³, Romain Quidant^{4,5}, and Lukas Novotny¹

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³ Faculty of Physics, University of Vienna (Austria), ⁴ The Barcelona Institute of Science & Technology, ICFO – Institut de Ciències Fotoniques (Spain), ⁵ ICREA—Institució Catalana de Recerca i Estudis Avançats (Spain)

Recent progress in optomechanics, or the coupling of a mechanical resonator to a laser field, has demonstrated an unprecedented level of optical precision and control, heralding a new generation of photonic sensors. Despite remarkable advances in nano-fabrication, clamping losses dominate many oscillators' intrinsic dissipation and limit mechanical Q-factors and thereby the achievable force sensitivity. Overcoming clamping losses via levitation, we present an optically tweezed nanoparticle as a viable photonic force sensor whose $Q \sim 10^9$ is limited by the shot noise of photons.

The momentum transfer between a photon and an object defines a fundamental limit for the precision with which the object's position can be continuously measured. If the object oscillates at a frequency Ω_0 , measurement backaction adds quanta $\hbar\Omega_0$ to the oscillator's energy at a rate Γ_{recoil} , a process called photon recoil heating. Here, we use an optically levitated nanoparticle in ultrahigh vacuum to directly measure Γ_{recoil} . Using a phase-sensitive feedback scheme, we cool the harmonic motion of the nanoparticle from ambient to microkelvin temperatures and measure its reheating rate under the influence of the radiation field. The recoil heating rate

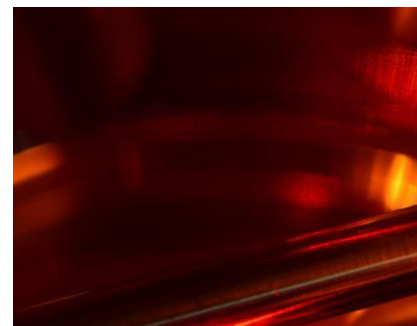


Fig. An optically-tweezed nano-particle in ultra-high vacuum illuminated by a red-laser beam.

is measured for different particle sizes and for different excitation powers, without the need for cavity optics or cryogenic environments.

The measurements are in quantitative agreement with theoretical predictions and provide valuable guidance for the realization of quantum ground-state cooling protocols. Improving measurement sensitivity enhances the stability of feedback control and reduces the nanoparticle's natural fluctuations to 30 pm, or less than one Bohr radius. With such optomechanical control, we estimate a force sensitivity on the order of $zN/Hz^{1/2}$, which could be used for the measurement of weak, near-field forces.

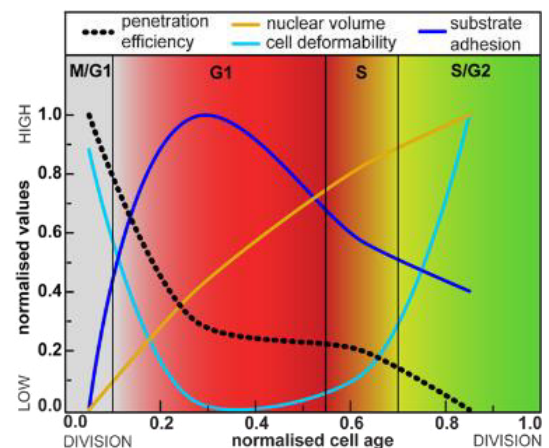
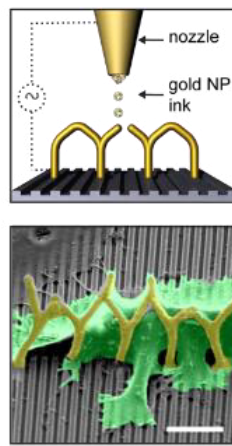
[1] V. Jain, et al., *Phys. Rev. Lett.* **in press** (2016)

Paramorphotic Youth: A 3D Nanoprinted Model Unveils a New Mechanism of Cancer Cell Migration

Magdalini Panagiotakopoulou¹, Martin Bergert¹, Anna Taubenberger², Jochen Guck², Dimos Poulikakos^{1*}, and Aldo Ferrari^{1*}

¹ *Thermodynamics in Emerging Technologies, D-MAVT, ETH Zurich*, ² *Biotec TU Dresden (Germany)*

Metastatic progression of tumours requires the coordinated dissemination of cancerous cells through interstitial tissues and their replication in distant body locations. Despite their importance in cancer treatment decisions, key factors, such as cell shape adaptation and the role it plays in dense tissue invasion by cancerous cells, are not well understood. Here, we employ a 3D electrohydrodynamic



nano-printing technology to generate vertical arrays of topographical pores that mimic interstitial tissue resistance to the mesenchymal migration of cancerous cells, in order to determine the effect of nuclear size, cell deformability and cell-to-substrate adhesion on tissue invasion efficiency. The high spatial and temporal resolution of our analysis demonstrates that the ability of cells to deform depends on the cell cycle phase, peaks immediately after mitosis and is key to the invasion process. Thus, our results support a novel mechanism in which cell proliferation and pore penetration are functionally linked to favour the interstitial dissemination of metastatic cells.

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ABSTRACTS OF POSTERS

1 Magnetically-Triggered Crack Healing of Bituminous Materials Using Iron Oxide Nanoparticles

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Healing of micro-cracks is crucial for a recovery of the mechanical properties of bituminous materials resulting in a lifetime expansion. However, such process is often challenged by the efficiency of the additives, the repeatability of the process or its feasibility for large-scale applications. In this

study, we propose a new method to close micro-cracks by using magnetic nanoparticles as heating agents. Upon the presence of an external magnetic field, magnetic nanoparticles have the particularity to produce heat. When mixed with a thermoplastic material such as bitumen, the generated heat warms up their surroundings and eventually decreases the viscosity of the material.¹ Here, iron oxide nanoparticles are functionalized by oleic acid to enable homogeneous distribution of nanoparticles in bitumen and then subjected to an external magnetic field. The results show that $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles with a mean crystallite size of 50 nm exhibit the Specific Absorption Rate values of 285 W/g through a mechanism predominated by hysteresis losses. In contrast to the inefficient heating rate of electrically-conductive additives, we find that heating of pre-embedded iron oxide nanoparticles in bitumen allows the closure in few seconds of micro-cracks created by Vickers indentation, thus opening a new efficient way to heal micro-cracks in road pavements in the presence of mineral aggregates.²

[1] C. Corten et al., *Adv. Mater.* **21**, 48 (2009); [2] E. Jeoffroy et al., *Constr. Build. Mater.* **112** (2016)

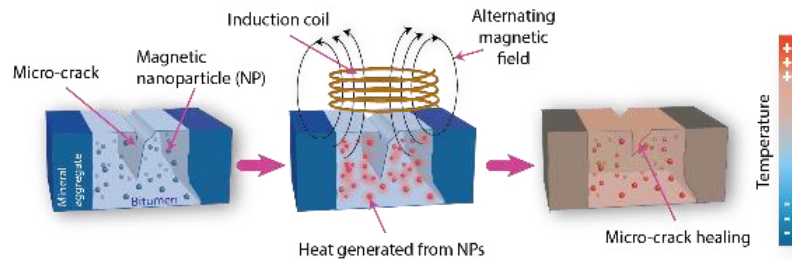


Fig. Schematics illustrating the proposed crack healing method for bituminous materials using iron oxide nanoparticles embedded in bitumen.

2 Cohesive Properties of Ultrathin $\text{Ge}_2\text{Sb}_2\text{Te}_5$ Films on Polyimide Substrates

Franziska Schlich, Henning Galinski, and Ralph Spolenak

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Ultrathin $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) films are applied in optical data storage and they are promising candidates for flexible display applications. A loss of integrity of these thin brittle films may lead to failure of the device. Hence there is a strong interest in investigating the mechanical properties of GST films: the onset strains of fragmentation of 20 nm-400 nm thick as-deposited amorphous and crystalline GST films were determined by in situ resistance measurements, optical microscopy and reflectance anisotropy spectroscopy (RAS) during uniaxial tensile loading. By comparing the results of the applied methods RAS was introduced as a promising tool to determine the onset strain of fragmentation of brittle films. The fracture strength and fracture toughness of the films were calculated. Amorphous GST fractures at larger strains than crystalline GST. However, due to the small Young's modulus it is less tough than crystalline GST.

The results are critically discussed and compared to other thin brittle films.

3 Composites Reinforced via Mechanical Interlocking of Surface-Roughened Microplatelets within Ductile and Brittle Matrices

Davide Carnelli, Rafael Libanori, and André R. Studart

Complex Materials, D-MATL, ETH Zurich

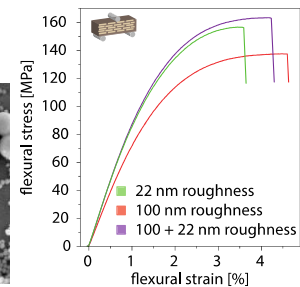
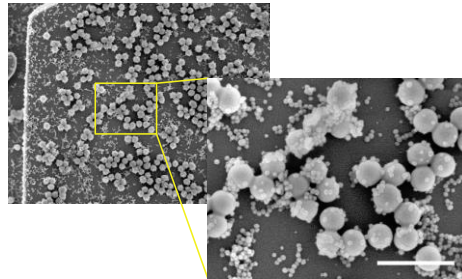
Load-bearing reinforcing elements in a continuous matrix allow for improved mechanical properties and can reduce the weight of structural composites. As the mechanical performance of composite systems are heavily affected by the interfacial properties, tailoring the interactions between matrices and reinforcing elements is a crucial problem. Recently, several studies using bio-inspired model systems suggested that interfacial mechanical interlocking is an efficient mechanism for energy dissipation in platelet-reinforced composites. While cheap and effective solutions are available at the macroscale, the modification of surface topography in micron-sized reinforcing elements still represents a challenging task. Here, we report a simple method to create nanoasperities with tailored sizes and densities on the surface of alumina platelets and investigate their micromechanical effect on the energy dissipation mechanisms of nacre-like materials. Composites reinforced with roughened platelets exhibit improved mechanical properties for both organic ductile epoxy and inorganic brittle cement matrices. Mechanical interlocking increases the modulus of toughness (area under the stress-strain curve) by 110% and 56% in epoxy and cement matrices, respectively, as compared to those reinforced with flat platelets. This interlocking mechanism can potentially lead to a significant reduction in the weight of mechanical components while retaining the structural performance required in the application field.

4 Hierarchically Roughened Microplatelets Enhance the Strength and Ductility of Nacre-Inspired Composites

Tobias P. Niebel, Davide Carnelli, Marco R. Binelli, Rafael Libanori, and André R. Studart

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Rough interfaces featuring nanoscale asperities play a major role in the mechanics of nacre, the inner layer of some mollusk shells. To gain further insights into the effect of asperity size, hierarchy and coverage on the mechanics of artificial nacre-inspired composites, we decorate alumina microplatelets with silica nanoparticles of selected sizes and use the resulting roughened platelets as reinforcing elements (15 vol%) in a commercial epoxy matrix.



For a single layer of silica nanoparticles on the platelet surface, increased ultimate strain and toughness are obtained with a large roughening particle size of 250 nm. On the contrary, strength and stiffness are enhanced by decreasing the size of asperities using 22 nm silica particles. By combining particles of two different sizes (100 nm and 22 nm) in a hierarchical fashion, we are able to improve stiffness and strength of platelet-reinforced polymers while maintaining high ultimate strain and toughness. Our results indicate that carefully designed hierarchically roughened interfaces enable the deformation of a larger fraction of the polymer matrix. This design concept improves the mechanical response of bioinspired composites and can possibly also be exploited to enhance the performance of conventional fiber-reinforced polymers.

[1] T.P. Niebel et al., *J. Mech. Behav. Biomed. Mater.* **60**, 367 (2016)

5 Effect of Ion Species on Deformation Behavior of Aluminum Micropillars Produced by Focused Ion Beam Machining

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Focused ion beam technology is the primary method for manufacturing sample geometries for micromechanical testing, e.g. micropillar compression. However, the possible effect of the gallium ions on metals known to be embrittled by liquid metal gallium is unknown. In this work, both xenon and gallium ions were used to fabricate micro-compression samples from single crystalline and ultrafine-grained aluminum. The different ion species has little effect on the yield strength of single crystalline aluminum. However, for the ultrafine-grained aluminum, the Ga ions appears to reduce mechanical strength proportional to both the Ga implantation dose and the grain boundary content.

6 The Role of Mineral Contacts in Nacre-Like Polymer-Matrix Composites

Madeleine Grossman, Florian Erni, Florian Bouville, Rafael Libanori, and André R. Studart

Complex Materials, D-MATL, ETH Zurich

The rational design of composites with high strength, modulus and fracture toughness is a major challenge in materials science. Fracture toughness requires inelastic deformation and ductile response but the molecular origins of strength conflict with ductility [1]. Yet, nature works around this inherent conflict, creating composites with hierarchical meso-structures that are stiff in their pristine state but become inelastic after damage. Nacre, aka mother of pearl, materializes this concept by arranging mineral platelets and bio-polymers layers like bricks and mortar. During damage, toughening mechanisms engage at the interfaces between platelets, allowing them to dissipate energy over a large volume, called a process zone. Optimal morphology and interfacial strength between platelets appears to be key to nacre's functionality, but previous methods for producing nacre-like composites were unsuited for exploring these parameters. To address this issue, a new process, Vacuum Assisted Magnetic Alignment (VAMA,) was developed to quickly and reproducibly pack mineral micro-platelets into an aligned brick and mortar structure, and sintering under external pressure consolidated these platelets into a nacre-like mineral scaffold. Using commercially available titania-coated alumina microplatelets creates the opportunity to tune the strength of the platelet-platelet interfaces: since titania sinters at significantly lower temperatures than alumina, variation of the sintering temperature modulates the size of titania inter-platelet contacts. Infiltrating these mineral scaffolds with toughened epoxy yields series of composites with a wide range of mechanical properties: the flexural moduli range from 90 to 180GPa and flexural strength within 270-370 MPa. As the interfacial mineral contacts approach their optimum strength, the composite's resistance to fracture initiation, K_{IC} , increases up to 50%, but beyond this optimum, the composite becomes more brittle. These results support the hypothesis that optimized mineral contacts between platelets are of central importance to nacre's combination of strength, modulus and toughness.

[1] R.O. Ritchie, *Nature Materials* 10, 817 (2011)

7 When Nanoparticles Meet Poly(Ionic Liquid)s: Chemoresistive CO₂ Sensing at Room Temperature

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Tetraalkylammonium-based poly(ionic liquid)s (PILs) are able to absorb particularly large amounts of CO₂; thus, they are considered up-and-coming materials in applications ranging from sensing, separation, to storage of CO₂. To meet the requirements of practical usage, their chemical activity has to be combined with other functionalities, for example, by fabricating composite materials. Poly[(*p*-vinylbenzyl)trimethylammonium hexafluorophosphate] and La₂O₂CO₃ nanoparticles - both of which are intrinsically insulating materials - are utilized as building blocks, taking full advantage of the electrostatic interaction at their interface to boost the overall conductivity of composites at room temperature. To rationalize this unique behavior, the charge transport mechanism is studied using impedance spectroscopy. It is found that, for the composites with La₂O₂CO₃ content of 60–80 wt%, the interfacial effect becomes dominant and leads to the formation of conduction channels with increased mobility of [PF₆]⁻ anions. These composites show further increase of the conductivity when exposed to pulses of CO₂ between 150 and 2400 ppm at room temperature in a relative humidity of 50%. This work therefore provides a simple strategy to achieve an enhancement of the electrical properties required for the utilization of PILs-based CO₂ sensors, but in the future this concept can be easily extended to other electronic devices.

8 Towards Marangoni-Driven Colloidal Deposition

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Fabrication of thin films is an extremely valuable tool in the creation of surfaces with designed functional prop-

erties, derived from controlled roughness, periodicity or structure. Examples of applications include anti-reflect coatings, planar waveguides or transparent conducting films. The classical Langmuir-Blodgett method of deposition of molecular or colloidal species at fluid interfaces offers a lower cost and environmentally gentler procedure compared to gas-phase methods often employed industrially, however, by being driven by a physical barrier compression the process is difficult, if not impossible to scale up. This work investigates the use of Marangoni flows, generated by small temperature gradients across the interface, combined with rheological insights, to transport interfacial material at constant surface pressure, thereby working towards the development of a scalable, continuous deposition process at liquid interfaces.

9 Electrochemical Additive Manufacturing of Metals at the Nano-Scale

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Additive manufacturing (AM) is changing the way we design and manufacture components. AM frees the design from the significant constraints imposed by subtractive manufacturing techniques and thus allows to construct for best function and not easiest manufacturing. Traditional AM of metallic materials is an established industrial processes by now. However, because the resolution of the applied techniques is typically 100 micrometer, these techniques are not suited for micro- or even nano-manufacturing. However, design limitations of traditional microfabrication techniques are even more severe than these of their macroscopic counterparts. Hence, AM at small length scales can be expected to change fabrication-processes even more severely than at the macroscale.

Several AM techniques for metals at the microscale have been proposed, and each technique has its advantages and disadvantages. The fabricated geometries can range from simple 2.5D to overhanging, complex, true 3D structures, achievable resolutions range from tens of nanometers to several micrometers and the purity of the deposit varies between tens of volume-percent to pure metal.

Here, we present a new technique based on electrochemical deposition. Schuster et al. [1] have shown that nanosecond-voltage pulses can strongly localize electrochemical reactions. We utilize this concept to deposit 2D and simple 3D cobalt structures in an electrochemical scanning-tunneling-microscope. We achieve a resolution of ~50 nm. At this stage, we assume that the deposits are dense, pure metallic cobalt. If so, our approach is the AM technique with the best resolution that easily synthesizes pure, dense metallic structures.

[1] R. Suster et al., *Science* **289**, 98 (2000)

10 Highly Luminescence Colloidal Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X=Cl, Br, and I): The Path from Synthetic Methodologies to Lasing Studies

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Chemically synthesized inorganic nanocrystals (NCs) are considered to be promising building blocks for a broad spectrum of applications including electronic, and photovoltaic devices. Using inexpensive commercial precursors, we have synthesized fully inorganic cesium lead halide perovskites (CsPbX₃, X=Cl, Br, and I or Cl/Br and Br/I) in the form of monodisperse colloidal nanocubes (Fig. 1).¹ Through compositional modulations, their bandgap energies and emission spectra are readily tunable over the entire visible spectral region. The photoluminescence of CsPbX₃ NCs is characterized by narrow emission line-widths, wide color gamut covering up to 140% of the NTSC color standard, high quantum yields of up to 90% and radiative lifetimes in the range of 4-29 ns.¹ While cation-exchange is facile and commonplace, anion-exchange reactions have not received substantial deployment. Furthermore, fast inter-nanocrystal anion-exchange is demonstrated, leading to uniform CsPb(Cl/Br)₃ or CsPb(Br/I)₃ compositions simply by mixing CsPbCl₃, CsPbBr₃ and CsPbI₃ nanocrystals in appropriate ratios.²

Inspired by the highly efficient photoluminescence, we tested CsPbX₃ NCs as inexpensive optical gain medium. We observed that room-temperature ultralow-threshold amplified spontaneous emission can be obtained

in the whole visible spectral range with low pump thresholds down to $5 \pm 1 \mu\text{J cm}^{-2}$ and high values of modal net gain of at least $450 \pm 30 \text{ cm}^{-1}$.³

[1] L. Protesescu et al., *Nano Letters* **15**, 3692 (2015); [2] G. Nedelcu et al., *Nano Letters* **15**, 5635 (2015); [3] S. Yakunin et al., *Nat. Commun.* **6**, 8056 (2015)

11 Investigating the Surface Charge of Wood by Streaming Current and Streaming Potential Measurements

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The goal of this work is to obtain an in-depth knowledge about the interfacial charges of wood in an aquatic environment. Wood as natural and complex material is chemically and morphologically heterogeneous. In particular, its hydrophilic character along with the anisotropic porosity and roughness of wood surfaces pose a challenge when investigating its surface charge. We measured different wood surfaces by streaming current and streaming potential measurements and applied selected physical models to calculate the zeta potential. For instance the Helmholtz-Smoluchowski equation was used for streaming current measurements on radial surface planes with an adjustable gap cell whereas the Fairbrother-Mastin model was used for streaming potential measurements in a cylindrical cell containing wooden disk samples. Zeta potential measurements as a function of pH and ionic strengths of various wood species were conducted to compare the net surface charge among different wood species. In a second part, the measurement technique was applied to modified wood surfaces. The adsorption of polyelectrolytes on wood surfaces was studied to support the understanding of a layer-by-layer coating process. Alternating layers of cationic and anionic polyelectrolytes were deposited and measured by streaming current measurements which showed the reversal of the surface charge polarity for each applied layer.

12 Particle Detachment from Liquid-Fluid Interfaces: From Smooth towards Model Rough Particles

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Particle adsorption and self-assembly on fluid interfaces have attracted considerable attention as these phenomena can be exploited in Pickering-stabilized emulsions and foams,^{1,2} drug-delivery vehicles,³ mineral recovery by flotation,⁴ fabrication of nanostructured materials,⁵⁻⁶ to name a few applications. The main parameter controlling the particle interfacial behaviour is its three-phase contact angle ϑ , which defines wetting and affects both self-assembly and particle dynamics at the interface. Furthermore, inter-particle interactions, e.g., capillary⁷ that arise due to interfacial deformations around each particle, depend on particle wettability, i.e. on ϑ . In this work, using colloidal-probe AFM, we measure the contact angles of non-modified and hydrophobised silica spheres at air-water / oil-water interface. The experimental data are analysed using a detailed and self-consistent theoretical model, which relates ϑ to various measurable quantities. It turns out that our model can predict the force-distance curve for the process of particle retraction without any adjustable parameters. To verify our results for ϑ , we compare them to contact angle measurements from independent methods such as GTT⁸, FreSCa⁹. The excellent agreement proves that our analysis is valid and can be used successfully to determine ϑ . This exquisite tool can be used to study the up-to-now unexplored adsorption/desorption behaviour of model rough particles relevant for applications.

[1] S. U. Pickering, *J. Chem. Soc., Trans.* **91**, 2001 (1907); [2] R. Aveyard et al., *Adv. Colloid Interface Sci.* **100-102**, 503 (2003); [3] A. D. Dinsmore et al., *Science* **298**, 1006 (2002); [4] A. V. Nguyen et al., in *Colloidal Particles at Liquid Interfaces*, ed. B. P. Binks and T. S. Horozov, Cambridge University Press, Cambridge, 1st ed., Chapter 9, 328-382 (2006); [5] A. Böker et al., *Soft Matter* **3**, 1231 (2007); [6] R. McGorty et al., *Mater. Today* **13**, 34

(2010); [7] P. A. Kralchevsky and K. Nagayama, *Langmuir* **10**, 23 (1994); [8] V. N. Paunov, *Langmuir* **19**, 7970 (2003); [9] L. Isa et al., *Nat. Commun.* **2**, 438 (2011)

13 Magnetic Field Induced Ordering of Amyloid-Fe₃O₄ Hybrid Fibrils

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14 Revealing Near-Field Chirality in the Far Field

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Chiral structures, which are non-superimposable upon their mirror image, are essential in the selectivity of biological processes [1]. Thus, a great interest exists in enhancing the sensitivity of detection schemes for chiral molecules. The field of plasmonics offers a promising avenue to enhance biosensing applications, as metallic nanostructures induce highly concentrated electromagnetic near fields. When plasmonic structures have a chiral shape (e.g. spirals [2], helices [3] or chiral pyramids [4]) they can greatly enhance the selectivity of chiral sensing applications by inducing intense, highly twisted chiral near fields. However, to date no direct experimental method exists to quantify the chirality of these fields and thereby assess the potential of a nanostructure for the aforementioned applications.

Here, we present a theoretical framework [5] that identifies the optical chirality flux as an ideal physical quantity to meet this goal. Our study shows that the optical chirality flux scattered into the far field of a structure provides valuable information on its highly twisted near fields. Further, we demonstrate that the optical chirality flux is a measurable quantity due to its close connection to the degree of circular polarization. This opens the door to the effective design and evaluation of chiral plasmonic nanostructures for chiroptical applications.

[1] A. Roger and B. Norden, *Oxford University Press* (1997); [2] M. Schäferling et al., *Phys. Rev. X* **2**, 031010 (2012); [3] J. K. Gansel et al., *Science* **325**, 1513 (2009); [4] K. M. McPeak et al., *Nano Lett.* **14**, 2934 (2014)

15 X-Ray Magnetic Scattering in Thermally Active Artificial Spin Ice

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Artificial spin systems consist of mesoscopic single domain magnetic islands arranged on a two-dimensional lattice and coupled via magnetostatic interactions. Such systems have attracted considerable interest due to their complex magnetic phase diagrams [1] and moment excitations resembling emergent magnetic monopoles [2]. We apply X-ray Resonant Mag-

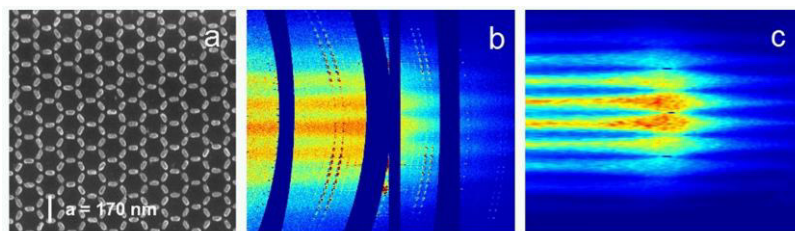


Fig. (a) SEM image of the artificial kagome spin ice with sub-70 nm islands. (b) Experimental scattering pattern from artificial kagome spin ice obtained at Fe L₃ edge [6]. (c) Numerical calculation of the magnetic scattering pattern using moment configurations from Monte Carlo simulations. Magnetic scattering is well reproduced indicating kagome ice I magnetic phase [6].

netic Scattering, measured at the RESOXs endstation of the SIM beamline at the Swiss Light Source, to look at

zero-field magnetic correlations in thermally active artificial kagome spin ice, see Fig. a. The energy of circularly polarized X-rays was tuned to the Fe L3 absorption edge, yielding sensitivity to the magnetisation. Magnetic diffuse scattering was measured at several temperatures above the blocking point of a thermally active artificial kagome spin ice (Fig. b) [6]. Experimental data can be understood using Monte Carlo simulations and subsequent numerical calculation of scattering patterns using kinematic scattering theory [3, 4, 5], see Fig. c. Magnetic diffuse scattering indicates zero-field ice-rule correlations of the kagome ice I phase with "two moments in – one moment out" and vice versa at each vertex [6]. They are reminiscent of the correlations in atomic spin ice that produce magnetic diffuse scattering with pinch points or bow ties [7].

[1] G. Möller and R. Moessner, *Phys. Rev. B* 80, 140409 (2009); [2] E. Mengotti et al., *Nature Physics* 7, 68 (2011); [3] M. Blume et al., *Journal of Applied Physics* 8, 3615 (1985); [4] J. P. Hannon et al., *Phys. Rev. Lett.* 62, 2644 (1989); [5] J. Perron et al., *Phys. Rev. B* 88, 214424 (2013); [6] O. Sendetskyi et al., submitted (2016); [7] T. Fennell et al., *Science* 326, 415 (2009)

16 Magnetic Bistability in Single Atoms

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For decades, the smallest known systems showing slow relaxation behavior have been polynuclear and mono-nuclear metal-organic complexes, so-called single-molecule magnets (SMM) [1]. Beyond SMM, the ultimate limit of magnet size shrinkage is an isolated magnetic atom on a nonmagnetic substrate. However, since the report of giant magnetic anisotropy in individual magnetic atoms on surfaces [2], the observation of magnetic remanence in single adatoms has remained an elusive goal, since the coupling- i.e. energy and angular momentum exchange, of the magnetic moment to the environment occurred on a timescale in the pico- to microsecond range, i.e. much faster compared to magnetization loop measurements. The key to stabilize the single magnetic moment of an adatom is therefore to develop a viable route for minimizing the coupling with the surrounding electronic/crystalline environment. We have recently achieved this goal for Ho atoms adsorbed on thin MgO(100) films on Ag(100), for which we measured a magnetic lifetime of 1500 s at 10 K and an open hysteresis loop with a coercive field of 3.7 T [3]. Magnetic remanence is observed up to 30 K, a temperature higher than typical SMM. The extraordinary magnetic bistability of the Ho/MgO system is attributed to the effect of (i) the mixing of odd J_z states in the ground state of Ho due to the C_{4v} symmetry of ligand field of MgO(100), which protects the magnetization from the reversal by quantum tunneling as well as by first-order electron scattering at zero and finite fields; (ii) the weak coupling to the electronic and (iii) vibrational degrees of freedom of the substrate ensured by the insulating and stiff MgO film.

[1] R. Sessoli et al., *Nature* 365, 141 (1993); [2] P. Gambardella et al., *Science* 300, 1130 (2003); [3] F. Donati et al., *Science* 352, 318 (2016)

17 How "Transparent" Is a Monolayer 2D Material to an Electric Displacement Field?

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Gate-tunable two-dimensional (2D) materials-based quantum capacitors (QCs) and van der Waals heterostructures involves tuning transport or optoelectronic characteristics by the field effect. Recent studies have attributed the observed gate-tunable characteristics to the change of Fermi energy in the first 2D layer adjacent to the dielectrics, while the penetration of the field effect through the one-molecule-thick material is often ig-

nored or over-simplified. We present a multiscale analysis to model penetration of the field effect through graphene in a metal-oxide-graphene-semiconductor (MOGS) QC, including quantifying the degree of “transparency” for graphene two-dimensional electron gas (2DEG) to an electric displacement field. We find that the space charge density in the semiconductor layer can be modulated by gating in a nonlinear manner, forming an accumulation or inversion layer at the semiconductor / graphene interface. The degree of transparency is determined by the combined effect of graphene quantum capacitance and the semiconductor capacitance, which allows us to predict the ranking for a variety of monolayer 2D materials according to their transparency to an electric displacement field as follows: graphene > silicene > germanene > WS₂ > WTe₂ > WSe₂ > MoS₂ > MoSe₂ > MoTe₂, when the majority carriers are electrons. Our findings reveal a general picture of operation modes and design rules for the 2D-materials-based QCs.

18 Photoemission Electron Microscopy Studies of Dynamics in Dipolar-Coupled Arrays of Nanomagnets

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Nanomagnets arranged in different geometries lead to unique energy landscapes with geometry specific properties. Given the flexibility in shaping the energy landscape, inspiration for array designs is drawn from a wide range of fields. Examples include nanomagnet chains for logic and complex arrays that display rich physics associated with frustration.

One of our primary areas of research is artificial spin ice [1], which consists of specific arrangements of nanomagnets that display analogous behavior to their real crystal counterparts such as the rare-earth Pyrochlore compounds. We have earlier investigated static/quasi-static responses of well-known structures, such as artificial square and kagome spin ices, and our current efforts are on probing for magnetization dynamics. Frustration, when combined with topological defects, leads to dynamics that are geometry specific [2]. We investigate the field-induced response of the nanomagnet arrays using Photoemission Electron Microscopy and, for the fast response, a femtosecond laser is used to excite the magnets with a magnetic field and, probe them at the nanosecond time scale by making use of the X-ray time structure provided by the synchrotron.

We are also investigating the control and propagation of magnetic states in dipolar-coupled nanomagnets for logic operations. Error free evolution of information in long chains of coupled nanomagnets continues to pose significant challenges, with a major limit being thermal fluctuations at room temperature and defects. We are investigating various schemes to mitigate such errors and to work close to the Landauer limit [3], which gives nanomagnets an added advantage over conventional forms of logic such as CMOS.

[1] L. J. Heyderman and R. L. Stamps, *J. Phys.: Condens. Matter* **25**, 363201 (2013); [2] D. Thonig and J. Henk, *J. Magn. Magn. Mater.* **386**, 117 (2015); [3] B. Lambson et al., *Phys. Rev. Lett.* **107**, 010604 (2011)

19 Structural Colors in Network Metamaterials

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The formation of color is one of the most direct physical observations, that can easily be made by eye and without laboratory equipment. The origin of color though can be manifold ranging from luminescence, fluorescence, strong and normal interference to structural color typical for biological systems. A prominent example of structural color in nature is the coloring of bird feathers, whose color does not originate from pigments but from the wavelength-selective interaction of light with network-based nanostructures on the feather barbs. In this work, we design and characterize a hybrid metamaterial, combining dealloyed subwavelength metallic networks with loss-less ultrathin dielectrics coatings. Using theory and experiments, we show how a sub-wavelength dielectric coating can be used to control the resonant coupling of light to localized plasmonic modes of the underlying nanomaterial. The designed metamaterial acts as a tunable highly efficient light trap in the visible, manifesting

in the formation of structural color. The network-like architecture of the nanomaterial allows for efficient absorption of light even at angles above 50°, and is characterized by a remarkable scratch resistance.

20 Spatial Manipulation of the Nonlinear Phase-Matched Light in Lithium Niobate Nanoscale Waveguides

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Controlling the directionality of the emission of light with nanoscale waveguides enables the possibility of engineering new nanophotonic integrated systems¹. Moreover, combining the control of the light direction with wavelength conversion using nonlinear optical properties will offer even more flexibility for compact designs.

Here we investigate nonlinear optical emission from lithium niobate nanowires (LiNbO₃ NWs), in particular second-harmonic (SH) generated signal. We show that the directionality of the waveguided SH can be shaped via modal design under phase-matching (PM) conditions, which is a pure nonlinear phenomenon.

We chose LiNbO₃ because of its large bandgap and low absorption in a wide range of wavelengths going from 350 nm to 5200 nm. Moreover, the confinement of visible linear light within the LiNbO₃ NWs due to their large refractive index difference and their sub-micron cross-sections permits a significant second-order response because the large nonlinear coefficients of this material. PM between the fundamental harmonic (FH) and the second-harmonic (SH) modes is achieved² and the SH response of the NW is significantly increased³.

The emission pattern of the nonlinear phase-matched light is measured using a multi-photon Fourier imaging technique. Identification of SH modes in the far-field (rather qualitative), i.e. not at the Fourier plane (more quantitative), has been recently carried out in GaP nanopillars⁴ (much shorter than NWs), therefore our quantitative study of the directionality of the nonlinear phase-matched emission from NWs is filling this gap.

[1] P. Pauzauskis et al., Nanowire photonics. *Mater. Today* 9, 36 (2006); [2] R. Geiss et al., Fabrication of nanoscale lithium niobate waveguides for second-harmonic generation. *Opt. Lett.* 40, 2715 (2015); [3] A. Sergejev et al., Enhancing Guided Second-Harmonic Light in Lithium Niobate Nanowires. *ACS Photonics* 2, 687 (2015); [4] R. Sanatnia et al., Modal Engineering of Second-Harmonic Generation in Single GaP Nanopillars. *Nano Lett.* 14, 5376 (2014)

21 Nanoparticle Detection in Heterodyne Common Path Interferometry

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Interferometry has been used to detect single immobilized gold nanoparticles in fluids with a size of 20 nm. The nanoparticles flow through a quartz nanochannel, illuminated with a strongly focused field polarizing the particle, which elastically scatters back a fraction of the light. The magnitude of the scattered field is proportional to the particle size. High sensitivity is required to differentiate particles with a small size difference of 10 nm.

The phase in the interferometric signal leads to a particle position uncertainty and broadens the particle size distribution. Heterodyne detection is a sensitive technique to measure the amplitude and the phase of the scattered electric field separately, leading to a narrower particle size distribution and higher measurement accuracy. In heterodyne interferometry, a standard modulator is used to modulate the frequency of the reference field. The modulator requires an extended interferometer path length, that leads to an amplification of the noise amplitude. We propose a simple technique of heterodyne interferometry in a stable, common path configuration where the vibration of a glass plate in the beam path leads to spectral side bands frequency-modulated reference field.

The goal is to build a compact and stable measurement device for ultrasensitive detection of various single nanoparticles in fluids, desired for various applications in biology and nano fabrication.

22 Tailoring Magnetic Anisotropy in the Hierarchical Wood Structure

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Wood possesses a hierarchical structure with outstanding mechanical properties, which constitutes an ideal scaffold for chemical modifications. Mineralization is one of the various methods to create a functionalized renewable biomaterial. The precipitation of ferri- and ferromagnetic mineral phases in the intrinsically anisotropic cell anatomy yields hybrid wood materials with direction-dependent magnetic properties, which have been characterized by hysteresis loops parallel and perpendicular to the cell axis.¹ Through a detailed characterization of the embedded magnetic phases using light and scanning electron microscopy, Raman spectroscopy, and X-ray diffraction techniques, it is possible to relate the nanocrystal composition, shape and size to the macroscopic magnetization of the modified wood samples. A variation of the chemical synthesis allows for tailoring the nanocrystallinity and aggregation state of the magnetic particles, as well as for their deeper insertion into the cell walls, resulting in higher degrees of magnetic anisotropy compared to previous studies. We foresee that such magnetic functionalization offers plenty of new opportunities for the application of wood-based biocomposites.

[1] V. Merk et al., *ACS Appl. Mater. Interfaces* **6**, 9760 (2014)

23 Structuring Light with Plasmonic Bull's Eyes

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Plasmonic antennas are able to confine electromagnetic fields at the nanoscale as well as shape the far-field pattern of coupled emitters. Thanks to these properties, they represent a powerful tool in a wide range of applications including optical imaging, light harvesting, and sensing [1]. Careful design of such nanostructures is necessary to enhance the in- and out-coupling efficiency of light and for matching the targeted wavelengths or propagation directions. Moreover, being able to predict and control both the polarization-dependent response of the plasmonic antenna and the polarization state of the outgoing light, offers a powerful perspective in manipulating the structure of electromagnetic fields [2], [3].

With the aim of controlling the spectral- and polarization-related properties of plasmonic antennas, we perform far-field numerical simulations and analyze the radiation pattern of plasmonic structures. Our focus is on plasmonic bull's eye apertures [4], that can demonstrate efficient light manipulation in sensing and photodetection [5] as well as thermal emission applications [6]. The impact of different geometrical features of the antenna and properties of the incoming light (e.g. wavelength and polarization) on the polarization state of the out-coupled light is investigated. We will correlate our results from simulations with experimental k-space results. Finally, recent work on multiresonant plasmonic antenna structures for advanced sensing applications will be presented.

Through our improved understanding of these structures, in terms of their response to polarized light and their polarizing properties, we will work towards polarimetric applications that may enable increased sensitivity and selectivity in plasmonic sensing.

[1] L. Novotny et al., *Nature Photonics* **5**, 83 (2011); [2] C. Osorio et al., *Scientific Reports* **5**, 9966 (2015); [3] F. Afshinmanesh et al., *Nanophotonics* **1**, 125 (2012); [4] H.J. Lezec et al., *Science* **297**, 820 (2002); [5] J. Schuller et al., *Nature Materials* **9**, 193 (2010); [6] S. Han et al., *Phys. Rev. Lett.* **104**, 043901 (2010)

24 Piezoelectric Nanogenerators with Flame-Made BaTiO₃

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Polycrystalline BaTiO₃ nanoparticles with diameter of 20-50 nm were made by Flame Spray Pyrolysis (FSP). The collected powders were characterized by BET, XRD, SEM and Raman spectroscopy. The here made powders were embedded into nanocomposite films for piezoelectric nanogenerators. The voltage output of the nanogenerators were compared to ones containing commercial 64 and 278 nm BaTiO₃ nanoparticles. The time-averaged output voltage of nanogenerators containing flame-made 50 nm nanoparticles was 1.4 V, almost twice as high than that with commercial ones.

25 3D Metal Printing on the Micrometer Scale with a Force-Controlled Nanopipette

Luca Hirt¹, Alain Reiser², Ralph Spolenak², Janos Vörös¹, and Tomaso Zambelli¹

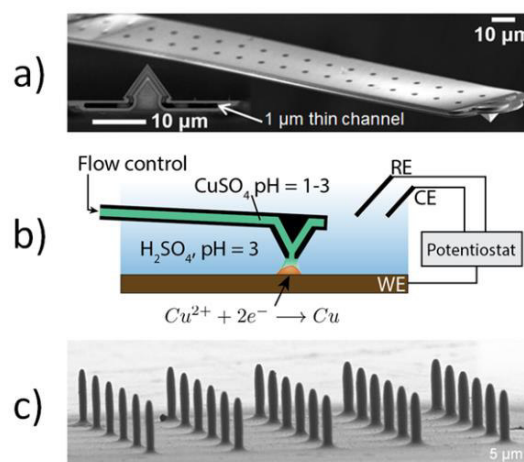
¹ Biosensors & Bioelectronics, D-ITET, ETH Zurich, ² Nanometallurgy, D-MATL, ETH Zurich

Additive manufacturing, with its advantages such as independence from photo masks, less material waste and freedom in geometry, is being increasingly adopted in industry. However, the most widespread 3D printing techniques have limited resolution and are not suitable for fabrication on the micro- and nanometer scale. This gap was filled by processes based on 2-photon polymerization with a resolution down to nanometers. For metals however, there is still no established solution for additive manufacturing on such small scales.

In our laboratory we are working with a unique tool – the FluidFM. This technology uses hollow atomic force microscopy (AFM) cantilevers to create a force-controlled micropipette (Fig. a). Thus, we have a system with the following features: We can precisely position a micropipette with an opening of 300nm, we can dispense liquid using a pressure controller, and we always know the forces acting on the micropipette since it is also an AFM cantilever.

Here, we show how we exploit this unique combination to create an automated metal 3D printer for the micrometer scale [1]. The technique is based on electrodeposition from a metal salt solution, which is provided locally from a FluidFM probe. Thus, the FluidFM tip serves as a local source of metal ions (Fig. b) which are electroplated in a confined area under the tip. The AFM force feedback allows us to automate the 3D printing: Whenever the growing structure touches the cantilever, this is sensed and the process may be continued at the next desired position. In this way, we can fabricate microstructures such as a regular pillar array (Fig. c) in a direct and mask-free manner.

[1] L. Hirt et al., *Advanced Materials* **28**, 2311 (2016)



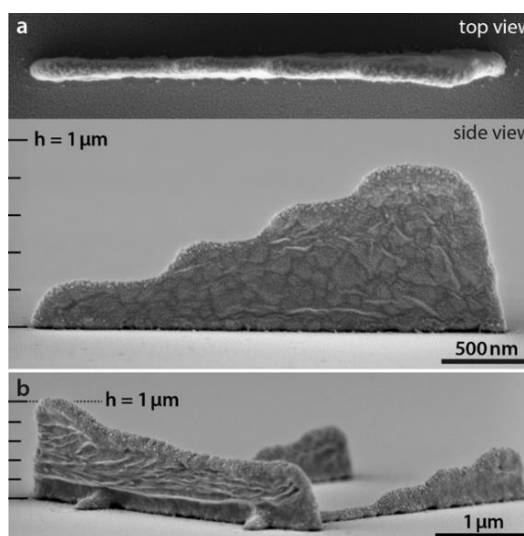
26 Electrohydrodynamic NanoDrip Printing of High Aspect Ratio Metal Grid Transparent Electrodes

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The transparent conducting electrode is an essential component in many contemporary and future devices, ranging from displays to solar cells. Fabricating transparent electrodes requires a balancing act between sufficient electrical conductivity and high light transmittance. Here we demonstrate the out-of-plane fabrication capability of the recently developed method of electrohydrodynamic NanoDrip printing to pattern gold and silver nanogrids with line widths from 80 to 500 nm, serving as excellent transparent conducting electrodes (TCEs).

In contrast to conventional ink-jet printing, the Electrohydrodynamic (EHD) printing technique allows the ejection of droplets more than one order of magnitude smaller than the nozzle opening. The printed structures automatically grow into the third dimension as the ejected droplets are guided by electrostatic autofocusing. The so-fabricated gold and silver nanowall grids are thermally annealed to render them electrically conductive. Built-up layer-by-layer through consecutive overprints, they reach an aspect ratio (AR = height-to-width ratio) of up to 7 for test structures and up to 4 for the actual TCE grids.



We report metal grid transparent electrodes with an optoelectronic performance of 8 Ω /sq sheet resistance at 94% relative transmittance. The very fine printed grid electrodes are invisible to the eye and yet show far better performance than conventional materials.

[1] J. Schneider et al., *Adv. Funct. Mater.* **26**, 833 (2016)

27 Tomographic Characterization of Lithium Deposits in Commercial Lithium Ion Battery Separators

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The formation of metallic lithium (Li) dendrites has major safety implications on current and future Li-based rechargeable batteries. Despite decades of research, the mechanisms and conditions of dendritic growth are still not well understood, as suitable test systems and characterization methods are challenging to develop. Theoretical efforts are underway and experimental studies have already established general conditions for Li plating [1]. However, these studies typically require specific materials and electrode geometries to enable optical access for in-situ analysis, and do not yet mimic the conditions in commercial batteries.

Dendrites causing failure of today's commercial Li-ion batteries grow within the pores of a polymeric separator. In addition to the electrochemical cycling and environmental conditions, the microstructure of the separator influences dendrite growth via electro-mechanical interfacial coupling. The transport parameters of electrolyte-filled separators depend on the overall cell pressure and local pore closure [2], and require multi-length scale analysis. Therefore, advanced characterization techniques to locate, visualize, and quantify dendrites within commercial separators with sub-micrometer resolution, as well as the separator microstructure itself, are needed to advance the understanding of dendrite formation and growth.

Here, we show focused ion-beam scanning electron microscopic (FIB-SEM) and x-ray tomographic analysis as complementary ex-situ characterization techniques. We demonstrate three-dimensional visualization and quantification of separator microstructures, and visualization of Li deposits grown in commercial separators following cycling in model cells (i.e., Li^0 |separator| Li^0 and Li^0 |separator|graphite) [3]. This separator microstructure data can be used for modeling mechanical and thermal properties, as well as transport phenomena of commercial Li-ion battery separators.

[1] C. T. Love, et al., *ECS Electrochem. Lett.* **4**, A24 (2015); [2] J. Cannarella and C. B. Arnold, *J. Electrochem. Soc.* **162**, A1365 (2015); [3] M. F. Lagadec et al., *J. Electrochem. Soc.* **163**, A992 (2016)

28 Charge Trapping for Ultra-Low Power Electronics beyond Conventional Limits

Alwin Daus¹, Christian Vogt¹, Niko Münzenrieder^{1,2}, Luisa Petti¹, Stefan Knobelspies¹, Giuseppe Cantarella¹, Giovanni A. Salvatore¹, and Gerhard Tröster¹

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29 Operando X-Ray Tomographic Microscopy on Lithium Ion Battery Graphite Electrodes

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Despite numerous studies presenting significant advances in imaging, analysis, and visualization of lithium ion batteries, graphite – the current state-of-the-art anode material for commercial applications, has found rather little attention in X-ray imaging studies so far.

Carbon's low core charge number results in weak X-ray attenuation contrast between graphite and the other

pore space filling components in an electrode microstructure, rendering data analysis challenging, unless staining techniques are applied. On the contrary, phase contrast based X-ray imaging methods facilitate the differentiation between different weakly absorbing materials, while still being applicable to electrochemically functioning batteries. In this work, we present the first *operando* propagation based phase contrast tomography study of graphite electrodes upon electrochemical (de)lithiation. Applying digital volume correlation techniques, we are able to capture the dynamic evolution of the electrodes during operation, quantifying local electrochemical activity, microstructural changes and strains throughout the electrodes as a function of 3D space and time.



30 Flexible A-IGZO Thin-Film Transistor Based UV-Sensors for Skin Health Applications

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31 Efficient Green-To-Blue Light Emitting Diodes Using 2D Organometal Halide Perovskites

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Colloidal suspension of two-dimensional (2D) organometal halide perovskites have shown ultimate potential to realize low cost, high-throughput, roll-to-roll fabrication of energy-efficient light-emitting diodes (LEDs). A number of approaches have been established to realize a color-tunable emission from perovskites, such as anion exchange, quantum confinement effect via size control synthesis of 2D perovskites. However, it is extremely challenging to realize a highly energy-efficient color-tunable emission from pure colloidal 2D perovskites based emissive layer because of their discrete film morphology that lead a poor charge transport and efficiencies. Here, we overcome this issue by doping colloidal dispersion of 2D methyl ammonium lead bromide (MAPbBr₃) perovskites with a typical molecular host, *N,N'*-dicarbazolyl-4,4'-biphenyl (CBP), to obtain efficient green-to-blue LEDs. Moreover, we demonstrate a facile synthesis route to produce stable colloidal MAPbBr₃ perovskites that exhibit a photoluminescence quantum yield (PLQY) from 50 to 92%. The resultant green perovskite LED exhibited an emission peak at 520 nm with a maximum external quantum efficiency (EQE) of 2.2%, a maximum power efficiency (η_p) of 6.3 lm W⁻¹, and a maximum current efficiency (η_c) of 8.0 cd A⁻¹. Taking blue perovskite LED for example, device showed an emission peak at 492 nm with a maximum EQE of 0.2%, η_p of 0.14 lm W⁻¹, and η_c of 0.2 cd A⁻¹. The resultant blue device revealed over 500 time higher EQE than that of the best blue organometal halide perovskite LED reported so far. The reason why the colloidal dispersion of 2D MAPbBr₃ emitters based devices demonstrated record high efficiencies may be attributed to three crucial factors, which are (i) high PLQY of 2D perovskite colloidal dispersion, and (ii) effective energy-transfer from CBP to MAPbBr₃ nano particles, (iii) CBP also provide a conductive matrix that can facilitate a homogeneous charge distribution within the emissive layer.

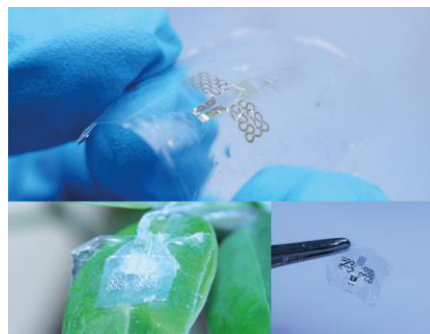
32 Stretchable Temperature Sensor That Biodegrades in the Environment

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¹ Wearable Computing, D-ITET, ETH Zurich

Due to massive worldwide problems of environmental pollution, like plastics in oceans, and waste recycling, biodegradable and compostable materials and devices gain more and more public attention. In the last years to avoid further pollution research in microfabrication was focusing on degradable materials and the underlying mechanisms and on producing first transient devices¹.

Here we present a fully biodegradable, flexible and stretchable temperature sensor with a resistive sensing element consisting of Magnesium. Magnesium is an extremely light-weight metal and shows great biocompatibility as it is resorbed by human body². A study on the dissolution of Magnesium revealed a high corrosion rate in physiological environment. This leads to the need of encapsulation of the device in order to extend its lifetime. Therefore biodegradable dielectrics such as silicon dioxide and silicon nitride and elastomers and polymers such as biodegradable ecoflex (from BASF, $E_{0.005} = 533\text{MPa}$), water-dissolvable polylactic acid (PLA) and gelatin ($E_{0.005} = 0.033\text{MPa}$) can be used.



In addition, the process of transfer printing allows us to transfer our microfabricated device to several substrates and therefore widening the range of applications from surface temperature sensors to implantable devices.

[1] S.-W. Hwang et al., *Science* **337** (2012) ; [2] X.-N. Gu et al., *Front. Mater. Sci.* **4**, 2 (2010)

33 Nano-Characterization by AFM for Investigating a LbL Coating Build-Up on Wood

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To establish wooden elements in the high class building sector, there is a need for less maintenance intensive, longer lasting, and invisible coatings. The Layer-by-layer (LbL) deposition is a well-known method to coat materials and to implement new functionalities. A nanoscale thin coating is build up due to electrostatic charges [1].

In a dipping process several layers with opposite charges are deposited onto the wood. Dipping experiments show that standard, short processing times on wood do not lead to a comparable homogeneous coating like reported in literature on standard material like quartz [2]. In a parameter study, the coating protocol was adapted to the rough, porous, and chemical heterogeneous wood surface.

Using wood as the substrate, common characterization techniques to monitor the build-up and performance of LbL-coatings show certain limitations. To understand the interplay between wood and coating, the coating topography and mechanics were characterized by Atomic Force Microscopy (AFM). In a comparative approach, the first bilayer build-up was studied in terms of adhesion and Young's Modulus using the Quantitative Imaging Mode. Thereby, a force distance curve was obtained in every pixel [3]. The visualisation of the nanoscale coating on the microscale rough wood is helpful to increase the understanding of the LbL parameters influencing the coating quality.

[1] G. Decher, *Science* **277**, 1232 (1997); [2] A. M. Lehalp et al., *Langmuir* **28**, 6348 (2012); [3] H.-J. Butt et al., *Surface Science Reports* **59**, 1 (2005)

34 Nd³⁺-Doped Nanophosphors for Bioimaging: Screening of Crystal Host Matrices

Pascal Gschwend, Fabian Starsich, and Sotiris E. Pratsinis

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35 Genetic Modification and Chemical Delignification of Poplar Wood to Prepare Hierarchically-Structured Cellulose Scaffolds for Functional Hybrid Materials

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Micro- and nano-fibrillated cellulose have recently been incorporated into various composite materials, due to their interesting mechanical properties and the diverse pathways for changing their surface chemistry.[1] However, as delignification processes requires large amounts of mechanical, thermal, and chemical energy, developing methods to facilitate these processes are of great industrial interest. One method that has seen a recent

surge in interest is genetic modification of various lignocellulosic materials to alter their chemistry to favor further processing.[2] Specifically, a well-known possibility to modify the polymeric structure of lignin in the wood cell walls, for the facile removal of lignin, is the RNA interference (RNAi) of cinnamyl alcohol dehydrogenase (CAD). While genetic modification may expedite the isolation of cellulose, which is already employed for pulp and paper production, it can also facilitate the removal of lignin for the preparation of hierarchically-structured cellulose scaffolds for functional hybrid materials. For controlled processing and well-defined scaffolds, it is important to monitor any chemical and structural changes to the resulting material. In the current study, common acidic and basic treatments, used in the production of wood pulp and paper, were performed on samples of genetically-modified and wildtype poplar trees. Chemical and structural analysis were carried out with FT-IR spectroscopy, confocal Raman spectroscopy, and X-ray diffraction. For both treatments, the delignification was faster and more complete for the genetically-modified samples, as compared to the wildtype wood. Although the acidic treatment showed no change in the structure of the crystalline cellulose, the basic treatment led to a change in the crystalline structure, which was more intense for the genetically-modified samples.

[1] Y. Habibi et al., *Chem. Rev.* **110**, 3479 (2010); [2] M. Baucher et al., *Crit. Rev. Biochem. Mol. Biol.* **38**, 305 (2003)

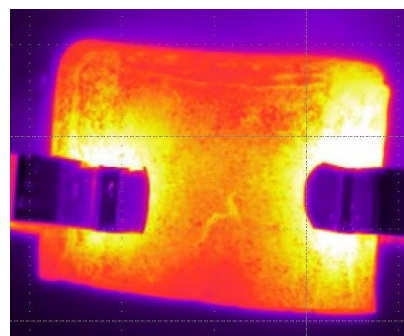
36 Graphene Wood: Mechanical, Electrical and Thermal Characterization of Plant Cell Based Nanobionic Materials

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Nanobionic materials are materials that combine biological constituents with synthetic nanostructures. This unique combination of constituents opens new pathways in the design of new materials with desired properties.

Synthetic nanostructures have been widely used to develop novel materials for engineering applications. Carbon-based nanostructures such as graphene and carbon nanotubes (CNTs) have been proven to enhance mechanical and electrical properties in composite materials. For example, an increase of tensile strength, Young's modulus and fracture toughness have been reported for polymer-based nanocomposites with graphene inclusions, compared to the pure host polymers. The combination of plant cells with carbon nanotubes has been shown to promote photosynthetic activity.



In our work, we combine undifferentiated plant cells with carbon nanotubes or graphene nanoplatelets to obtain novel composite materials that present mechanical properties similar to wood but are also electrically conductive and exquisitely temperature sensitive. We termed these new materials "cyberwood". In this poster, we present the influence of graphene nanoplatelets on the mechanical and electrical properties of cyberwood, and analyze the dependence of these properties on the concentration of nanoplatelets. We characterize the structure-function relation using synchrotron X-ray micro-tomography, to investigate the network arrangement of the nanoplatelets at the microscale. We also measured the thermal conductivity of the new material, to have a full comparison with other composite materials loaded with carbon-based nanostructures.

In addition to its remarkable mechanical, electrical and thermal properties, cyberwood is workable (like natural wood) but also moldable in any shape (like a polymer).

37 Wood Membrane for Oil-Water Separation

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Over the last years, the awareness over oil spill accidents in marine environment and aquatic ecosystems has

increased leading to tighter regulations. Novel strategies to separate oil-water mixtures from industrial wastewaters, polluted oceanic and river waters have become a global challenge. Given that traditional methods are limited with regard to their energy costs, low efficiency and complexity of the separation, new functional materials, which fulfil these restrictions are highly needed. We have been working with wood, which is a renewable material, to develop filters which are capable of separating oil from water. The hierarchical, porous structure of wood recalls the structure of the widely used separation membranes. Spruce, with a narrow distribution of cell lumen size (Figure 1A), is the perfect material for this application. By the combination of the natural structure of wood and the surface roughness (Figure 1B), generated by the cutting process, we have obtained a material with interesting wettability properties that is capable of separating oil from water. Moreover, the natural origin of the resource together with the low processing required makes this material both energy and cost efficient and highly competitive with other materials on the market.

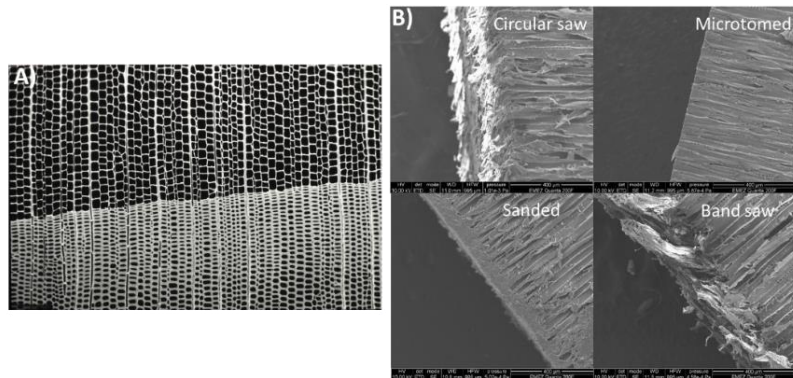


Fig. A) SEM picture of the microstructure of wood. B) SEM image of the profile obtained through different wood-cutting techniques.

38 Biocompatible 3-D Truss Structures with Controlled Mechanical Properties

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During the last decade, mechanical properties of engineered extracellular matrices (eECM) has been found to significantly influence cell behaviour and differentiation[1,2]. Such micro-environmental cues include structural stiffness, porosity and topology. Today's eECM can be generally classified into two types: homogeneous (with periodic structures) and heterogeneous (with non-periodic structures) [3]. Most studies on eECMs focus on periodic arrangements, and state of the art microstructural optimization is used to achieve desired properties. However, designing complex structural assemblies to achieve biomimetic designs is much more challenging and computationally expensive.

In our work we present a complete framework to generate eECM with spatially controlled mechanical properties. By combining our data-driven approach [4] with direct laser writing methods we can effectively fabricate such tailored eECMs for various applications in tissue engineering. As an example, we demonstrate that the controlled introduction of anisotropy into the design of eECMs facilitates the alignment of a HUVEC monolayer into a preferred direction.

This project is supported by the "Stiftung PROPTER HOMINES - Vaduz / Fürstentum Liechtenstein", the "Schwyzer-Winiker Stiftung" and the ETH Zurich Foundation. This work is part of the Zurich Heart project of Hochschulmedizin Zürich.

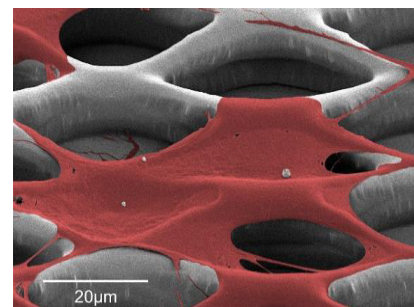


Fig. 1. HUVEC spanning over an anisotropic eECM with a unit cell dimension of $20\mu\text{m} \times 60\mu\text{m}$.

[1] D. Dado et al., *Semin. Cell. Dev. Biol.* **20**, 656 (2009); [2] R.H. Harrison et al., *Tissue Eng. Part B Rev.* **20**, 1 (2014); [3] S.M. Giannitelli et al., *Acta Biomater.* **10**, 580 (2014); [4] C. Schumacher et al., *ACM TOG* **34**, 136 (2015)

39 Formation and Characterization Horseradish Peroxidase Encapsulating Liposomes as Sensory Tool

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Unilamellar liposomes are widely used biomimetic systems for membrane studies or as drug carriers. Unfortunately, the fabrication methods of large unilamellar vesicles, which are defined as compartment surrounded by a single lipid bilayer with diameters of 100 to 1000 nm, are not well suited for encapsulation of macromolecules. This greatly hinders their use as nanoreactor systems because the encapsulation efficiency of functional hydrophilic enzymes is low^{1,2}.

In this work, we present a protocol for the encapsulation of Horseradish peroxidase (HRP) in large liposomes. Dried POPC was emulsified with enzyme containing buffer. Subsequent extrusion³ yielded a mixture of unilamellar vesicles and non-encapsulated HRP. We purified the HRP containing vesicles from free, un-encapsulated enzyme by gel permeation chromatography (Fig. B). Using the membrane impermeable HRP substrate 2,2'-azino-bis(3-ethylbenzo-thiazoline-6-sulphonic acid (ABTS) to demonstrate the selectivity of the liposomal HRP (data not shown). The activity of the HRP vesicles was measured with an ABTS after destroying the liposomes with amphiphilic cholate (see Fig. C) and with Amplex Red which is membrane permeable (Fig. D). Further, we demonstrate the use of liposomal encapsulated HRP as sensory tool in a simple microfluidic setup with a fluorescent read-out and determine the HRP encapsulation efficiency.

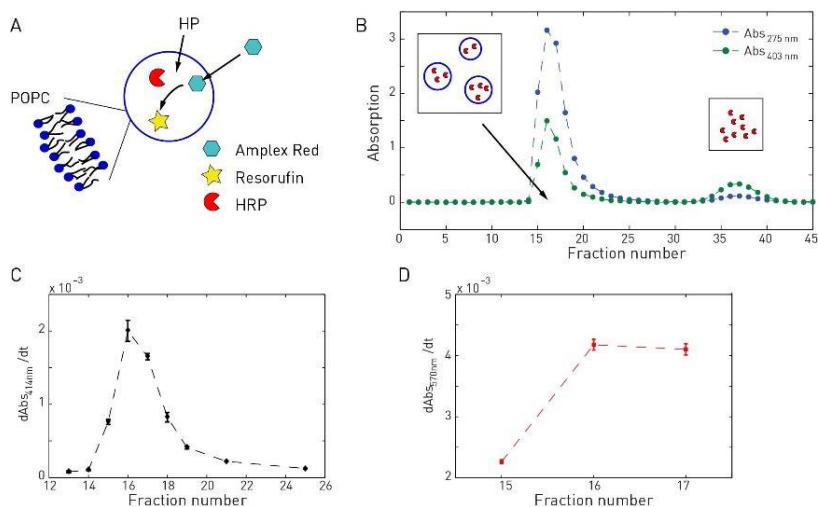


Fig. Horseradish peroxidase (HRP) encapsulating liposomes. A) Large POPC vesicles act as selective barrier for HRP substrates. Only membrane permeable substrates such as Amplex Red as well as hydrogen peroxide (HP) can permeate the membrane. B) Absorbance (shown at 275 and 403 nm) of fractions obtained by gel permeation chromatography of HRP vesicles. The first elution peak corresponded to the vesicles. The second elution peak showed an increased absorbance at 403 nm, specific for the heme group of HRP, and corresponded to free HRP. C) HRP activity measurements of vesicle fraction with ABTS. The vesicles were destroyed with cholate because ABTS could not permeate the membrane (data not shown). D) HRP activity measured with the membrane permeable Amplex Red. The activity trend was in accordance with the ABTS activity measurements in C).

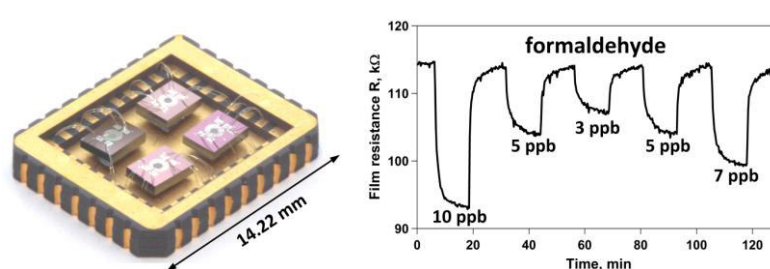
[1] M. Blocher et al., *Biotechnology and bioengineering* **62**, 1 (1999); [2] S. Hwang et al., *Colloids and Surfaces B: Biointerfaces* **94** (2007); [3] L.D. Mayer et al., *Biochimica et Biophysica Acta* **858**, 1 (1986)

40 Lung Cancer Detection from Breath? Portable E-Nose for Selective Low-ppb Formaldehyde Sensing

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¹ Particle Technology Laboratory, D-MAVT, ETH Zurich, ² Micro & Nanosystems, D-MAVT, ETH Zurich

Cancer is one of the major health problems of modern society with predicted 12.7 million newly diagnosed cases per year (2008).¹ Its early detection could significantly reduce morbidity and mortality. Formaldehyde (FA) is a potential breath marker for lung cancer.² It



typically occurs below 100 parts-per-billion (ppb) together with other gases at higher levels (e.g. acetone, NH₃, etc.) posing a sensitivity and selectivity challenge to current sensors. Here, we present a novel electronic nose (E-nose) for real-time quantification of FA in realistic gas mixtures. This E-nose consists of four nanostructured, highly porous Pt-, Si-, Pd- and Ti-doped SnO₂ sensing films (see Fig.).³ These offer stable and so far highest FA sensitivity down to 5 ppb (SNR > 30) at breath-realistic 90% relative humidity. Each dopant induces different analyte selectivity enabling *selective* detection of FA in gas mixtures by multivariate linear regression. In simulated breath, FA is detected with an average error ≤ 8.8 ppb, overcoming selectivity issues of single sensors. This device could facilitate easy screening of lung cancer patients.

[1] F. Bray et al., *Lancet Oncol.* 13, 790 (2012); [2] D. Fuchs et al., *Int. J. Cancer* 126, 2663 (2010); [3] A.T. Güntner et al., *ACS Sensors* in press (2016)

41 Density Gradients at Hydrogel Interfaces for Enhanced Cell Infiltration

Vincent Milleret^{1,2}, Ning Zhang^{3,4}, Benjamin R. Simona¹, Greta Thompson-Steckel³, NingPing Huang⁴, Janos Vörös³, and Martin Ehrbar²

¹ Ectica Technologies AG (Switzerland), ² Laboratory for Cell and Tissue Engineering, University Hospital Zurich, ³ Biosensors & Bioelectronics, D-ITET, ETH Zurich, ⁴ Southeast University Nanjing (China)

Hydrogels are the first choice class of materials to recreate in vitro the three-dimensional (3D) extra-cellular matrix environment (ECM). The cell encapsulation method is today the standard procedure to culture cells in hydrogels. This method consists in mixing the cells with the hydrogel liquid precursor and wait for this mixture to polymerize. Decoupling gel production and cell seeding is not possible with standard hydrogels, since cells plated on the surface of preformed hydrogels typically grow in a monolayer at the hydrogel surface. We developed a manufacturing process enabling the scalable production of hydrogels featuring an in-depth crosslinking density gradient at the hydrogel surface, directly in a microtiter plate format (3DProSeed™ well plate). The engineered gel-liquid or gel-gel interface is used to promote cell infiltration. The throughput is increased thanks to the possibility to obtain 3D hydrogel cultures by seeding cells in the same way as commonly done on 2D surfaces. In addition, it is now possible to seed different cell populations at different time points to develop advanced co-culture assays. Here we report the innovative fabrication method of the 3DProSeed plate and its application for cell-based assays, with relevance in the fields of oncology and neurotoxicology.

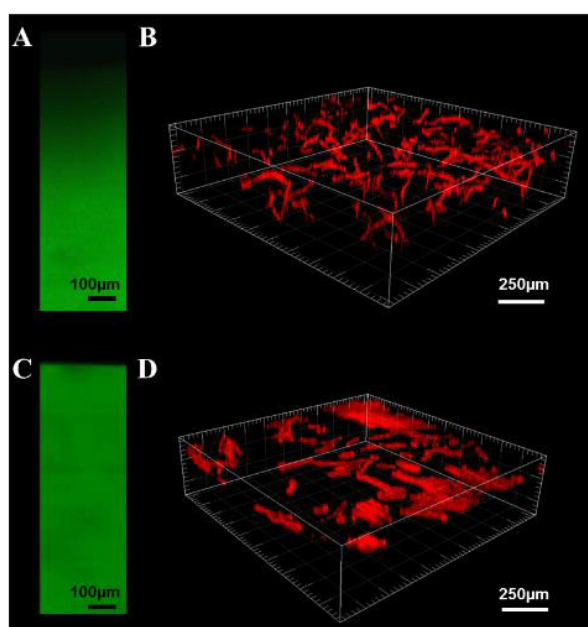


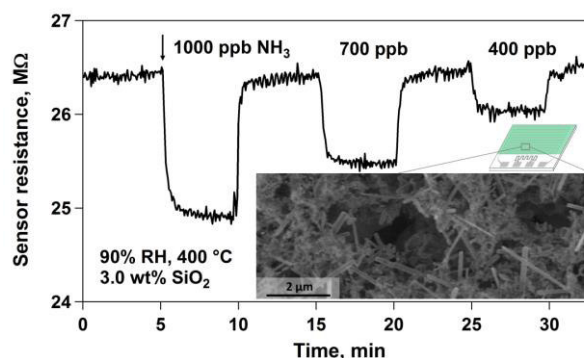
Fig. Hydrogels with surface crosslinking gradients (A) support cell invasion in 3D (B) whereas cells seeded on an homogeneous hydrogel (C) grow in 2D as a monolayer (D).

42 Kidney Disease Detection and Monitoring by Breath Analysis: Selective Sensing of NH₃ by Si-Doped α-MoO₃

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Ammonia is an important breath marker for non-invasive detection and monitoring of end-stage renal disease (ESRD). Here, a chemo-resistive gas sensor has been developed consisting of flame-made nanostructured α-MoO₃, a promising phase for selective detection of breath NH₃.¹ A key novelty is the thermal stabilization of α-MoO₃ by Si-doping that inhibits sintering and crystal growth at the operational conditions of such sensors. For *selective* NH₃ sensing the optimum SiO₂ content was 3 wt% and the operational temperature 400 °C. This sensor

showed superior NH₃ selectivity towards acetone, NO and CO, and accurately detected breath-relevant NH₃ concentrations down to 400 ppb at 90% relative humidity (see Fig.).¹ The corresponding response times (< 1 min) were sufficiently fast for on-line breath analysis. As a result, a stable and inexpensive sensor for NH₃ is presented which has the potential for early-stage diagnosis and monitoring of ESRD. This sensor can be readily integrated into a portable breath sampler.²



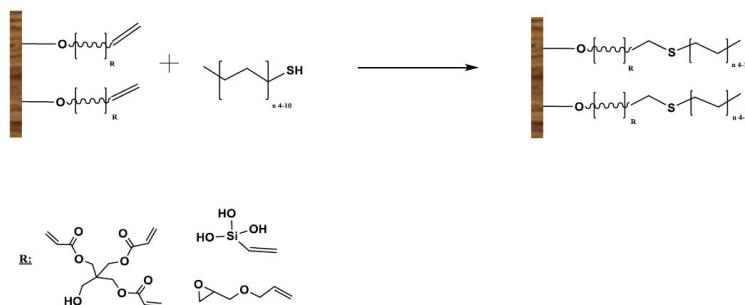
[1] A.T. Güntner et al., *Sens. Actuators B* 223, 266 (2016); [2] M. Righettoni et al., *J. Breath Res.* 9, 047101 (2015)

43 Click-Thiols as an Approach to Implement Novel Functionalities within Bio-Derived Scaffolds

Sanja Kostic^{1,2}, John K. Berg^{1,2}, Vivian Merk^{1,2}, Ingo Burgert^{1,2}, and Etienne Cabane^{1,2}

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As a result of dwelling fossil resources and pressing environmental issues, the utilization of sustainable materials gains more and more impact nowadays. Among various natural resources, wood and wood-based materials will certainly be an essential part of the future challenges. The benefits of this green material are ease of



processability, light weight, low cost, wide availability, excellent mechanical properties, and attractive appearance. In addition, wood possesses a unique hierarchical microstructure, which itself allows the design of future bio-derived materials. However, dealing with wood also bears some drawbacks, mainly due to its hygroscopic and anisotropic behaviour. Chemical modifications of the lignocellulosic scaffold are a simple yet versatile tool to alter wood properties.

In this work, Thiol-Michael additions were chosen as a promising candidate for a “grafting to” method to modify lignocellulosic materials. It was shown in our previous studies (using EDX mapping, Raman and FTIR) that acrylated wood can be modified by simple click thiol approach. Given the availability of more complex alkene containing structures (such as organosilane vinyl, polymer-brushes and dendrimers), there is a large potential for further modification by click-thiols. The structural and chemical anisotropy of the wood surface represents a challenge for the implementation of such a technique. We currently aim to develop a straightforward protocol in green conditions to adapt the approach to wood. While preserving the surface and the wood scaffold intact, the goal is to bring novel functionalities to the wood surface, such as superhydrophobicity through microstructuring inspired by plant surfaces. Such a modification would be highly desirable to protect wood from external aggressions.

44 Injectable, Self-Opening, and Freestanding Retinal Prosthesis

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Medtronic Chair in Neuroengineering, School of Engineering STI IBI-STI LNE, EPFL

This project exploits novel materials and concepts for the development and validation in-vitro, in-situ, and in-vivo of a biomimetic array of polymeric photoreceptors, implementing a combinatory strategy for the restora-

tion of large-field and high-resolution vision. Organic optoelectronic materials are patterned in arrays on elastic substrate, enabling a photo-voltaic stimulation and photo-thermal inhibition of retinal ganglion cells. These materials increase in surface potential and trigger neuronal firing upon illumination.

45 Microfluidic Hanging Drop Networks as a Versatile Experimental Platform for Spheroid Culturing and Analysis

Olivier Frey¹, Patrick Misun¹, Yannick Schmid¹, Saeed Rismani Yazdi¹, Felix Forschler¹, Axel Birchler¹, Sebastian C. Bürgel¹, Yin-Joung Kim¹, David A. Fluri², Wolfgang Moritz², Jens M. Kelm², Andreas Hierlemann¹

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We present a highly versatile integrated microfluidic platform for forming of and conducting experiments with multi-cellular spheroids. Multi-cellular spheroids are a frequent choice as 3D tissue models for a large variety of biological questions, in which a more realistic representation of an in-vivo-like situation is required. The platform consists of a fluidically interconnected hanging drop network, which unifies several functions into a single device: (i) parallel formation of multiple spheroids from same or different cell types (ii) conduction of developmental studies (e.g. stem cell differentiation) while modulating supply growths factors with flow, (iii) microfluidic dosage of defined substance concentrations to the spheroid models for drug testing, and (iv) implementation of continuous fluidic communication between different spheroid types to enable complex multi-organ models.

Multi-organ layouts, or so-called “body-on-a-chip” experimental setups, receive more and more interest as biomimetic in-vitro models in the context of systems biology and are highly relevant in drug discovery for the investigation of, e.g. complex compound pharmacokinetics. We, for example, could reproduce the effects of the cancer therapeutic prodrug cyclophosphamide, which in the human body first has to be activated by the liver before acting on cancer, by combining primary liver spheroids and a tumor spheroid on the same microchip. Conventional well cultures and discrete pipetting, in contrast, failed to reproduce these results. Further, the system is well suited to study endocrine effects that pancreatic islets exert on other tissue types (e.g. Liver) as physiological insulin concentrations in response to different glucose stimuli can be achieved in the continuously perfused chip loaded with a single islet spheroid. The platform is fully accessible for microscopy read-out equipped with precise liquid handling methods as well as integrated sensor systems (impedance spectroscopy and biosensors) and automated medium sampling for continuous monitoring.

46 Investigation of Permeation through Model Membranes in Single Vesicle Traps by Fluorescence Correlation Spectroscopy

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In this work, we present a two-layered microfluidic device that allows trapping, treatment, and analysis of up to 60 individual giant unilamellar vesicles (GUVs) or cells. The trapped objects can be exposed to chemical treatments like penetrating peptides, drugs, lysis buffers, antibodies, or staining dyes with precisely controlled durations while being constantly monitored with microscopic or spectroscopic methods. We use peptides that either partition into or penetrate across the membrane. Short polypeptides, in particular the HIV-1 trans-acting activator of transcription (TAT) domain and the nona-arginine (Arg-9) peptide possess the ability to cross natural cells as well as artificial membranes, enabling also cargo transport into the cells. Herein we focus on the permeability of model GUV membranes as a function of lipid composition, such as the percentages of charged or curvature-inducing lipids, or cholesterol. Permeation of the fluorescently labeled peptides into GUVs is then characterized with fluorescence correlation spectroscopy (FCS), which provides information on the intra- and extra-vesicular concentrations. With its single-molecule sensitivity, FCS, in combination with the microfluidic trap arrays, constitutes a valuable platform for drug or toxin screening.

47 Inverse-Opal Polypyrrole as Scaffold for Lithium-Sulfur Battery

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A polypyrrole scaffold is oxidative polymerized based on three-dimension ordered matrix (3DOM) of polystyrene sacrificial templates. The obtained porous scaffold could be applied to encapsulate and confine sulfur, serving as composite cathode for lithium-sulfur battery.

To build the porous structure, monodispersed polystyrene (PS) nanoparticles are prepared through dispersion polymerization and then gravimetrically self-assemble to 3DOM. Conductive polymer has attracted much interest in developing smart devices due to the advantages of flexibility, compatibility and processability. In our design, the polypyrrole (PPy) network is in situ synthesized via the infiltration of monomer to the prepared 3DOM template and oxidative polymerized in the presence of FeCl₃. The PS nanoparticles are removed by dissolving them in organic solvent, leaving space for accommodating sulfur. The obtained PPy scaffold shows a porous honeycomb structure. After infiltration of melted sulfur, secondary in situ polymerization of PPy is imposed to form a universal outer coating to efficiently encapsulate the inner composite within the open porous system and suppress the outward dissolution of polysulfide. PPy, as a typical conductive polymer, is selected as the conductive framework to support sulfur mainly based on the following considerations. Firstly, the nitrogen-rich PPy backbone is demonstrated to induce chemical adsorption of sulfur thus provide more active sites and facilitate the charge and ion transport. Secondly, PPy network has more mechanical flexibility compared with carbon, thus the structural deformation resulting from sulfur expansion is more alleviated. Thirdly, the PPy itself is electrochemically active for lithium intercalation/deintercalation.

Compared with other reported methods, our strategy can improve the overall conductive property, satisfy the basic requirement to accommodate the sulfur and confine the polysulfide species.

48 Cobalt-Based Catalysts for Oxidative Dehydrogenation of Ethane

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Ethene is an important feedstock in chemical industry used for the synthesis of polyethylene, ethylene dichloride, ethylene oxide and monoethylene glycol. It is typically produced by steam cracking of naphtha and ethane which requires high temperatures leading to severe coke deposition on the reactor walls, thus requiring periodic cleaning. Catalytic oxidative dehydrogenation of ethane (ODHE) can serve as an alternative to this process offering lower reaction temperature (< 800 °C) and higher ethene selectivity (> 70%). Although the reaction can be performed at much lower temperatures (< 500 °C) using O₂ as an oxidant, ethene selectivity is reduced due to the strong oxidizing nature of this oxidant [1]. Therefore, the use of a milder oxidant (e.g. CO₂) is preferred even though it requires higher reaction temperatures (> 600 °C). In this study, a wide range of single and mixed oxides supported cobalt catalysts were produced using a single step flame method and tested for the ODHE reaction [2]. The performance of the catalysts was strongly affected by the support type which could be attributed to the different structural and chemical properties of the catalysts characterized by various methods. Among all the supported catalysts, SiO₂, ZrO₂ and TiO₂-ZrO₂ supported cobalt catalysts showed similar ethene yield (~24%). However, in-depth analysis of these catalysts revealed that the performance of SiO₂ supported catalysts is superior (ethene yield ~ 34%, under non-optimized conditions) compared to others. Through material characterization, it was revealed that cobalt is present in different oxidation states depending on the support type indicating occurrence of different reaction pathways. More specifically, a non-redox reaction pathway is expected in SiO₂ supported catalyst where Co²⁺ is embedded in the SiO₂ matrix, while a redox mechanism (over CoO_x species) is proposed to be the dominant pathway over ZrO₂ and TiO₂-ZrO₂ supported catalysts.

[1] R. Koirala et al., *ACS Catal.* **5**, 690 (2015); [2] R. Koirala et al., *ACS Catal.* **submitted**, (2016)

49 Process Development for 100% Renewables-Based Polyethylene Furanoate (PEF) via Ring-Opening Polymerization

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Polyethylene furanoate (PEF), the promising 100% renewables-based substitute for fossil-based polyethylene terephthalate (PET), has successfully been synthesized by polycondensation, where conversion rate and molecular weight are limited by required condensation byproduct removal [1,2]. Ring-opening polymerization (ROP) can be a faster synthetic route to PEF, as cyclic monomers do not have end-groups and thus render byproduct removal unnecessary. We present ROP as a living chain-growth mechanism to deliver high conversion to PEF within minutes, featuring sufficiently high molecular weight for commercial applications such as bottles, textiles, medical grafts, etc. [3,4].

Bio-based cyclic PEF monomers (cyOEF) have been synthesized through different routes such as cyclodepolymerization of short PEF oligomers in 2-methylnaphthalene at yields >80% with a ring-size distribution from dimer to heptamer. The residual 20% linears can be recycled to increase overall yield. Purification from residual linears via silica gel adsorption to yield >99% cycles is essential for ROP to deliver 1) sufficiently high molecular weights, 2) reproducible reaction control and 3) whiter products.

cyOEF were successfully subjected to catalytic ROP to form PEF chains in yields of >95% within less than 20 minutes. Molecular weights equivalent to a PET bottle (~60'000 g/mol) were achieved using tin-catalysts such as FDA-approved tin octoate. The higher glass transition temperature (85°C vs. 73°C) and lower melting point compared with PET (215°C vs. 260°C) indicate higher thermal stability and easier processing of the final bottles. An at least 5x higher oxygen diffusion barrier complements the advantageous properties of ROP-derived PEF, which can be explained with a higher molecular rotational energy barrier as derived from molecular dynamics simulations.

[1] M. Gomes et al., *J. Polym. Sci. A: Polym. Chem.* **49**, 3759 (2011); [2] L. Sipos et al., *ACS Symposium Series* **1105**, P Smith(Ed.), 1 (2012); [3] D. Pfister et al., *Macromol Chem Phys* **216**, 2141 (2015); [4] J.-G. Rosenboom et al., **in preparation** (2016)

50 Sol-Gel Processed Multicomposite Nanostructured Hematite-Titania Photoanode with Improved Oxygen Evolution: The Role of the Oxygen Evolution Catalyst

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Solar energy conversion has emerged as a powerful and almost infinite source of energy. In the field of photoelectrochemical water splitting, the problem of energy storage in the form of electricity can be resolved through the direct conversion of water into its components hydrogen and oxygen which can be considered as byproduct in analogy to photosynthesis.

Recently, we have published detailed study in which we analyzed a composite Fe₂O₃-TiO₂ nanostructured photoanode. The preformed nanoparticles were obtained by the microwave-assisted nonaqueous sol-gel route.^{1,2} It became apparent that an active interface Fe₂TiO₅ was formed during the final annealing process, whereas TiO₂ itself was no longer detectable by means of XRD and HR-TEM analysis. Impedance measurements confirmed both a higher density of surface states and a higher carrier density as a function TiO₂.¹

Within this study, we included the application of a water oxidation co-catalyst coated on our nanocomposite photoanode, consisting of a ternary amorphous metal oxide with Fe and Ni as the main constituents and a third metal.¹ The greatest improvement could be achieved with the composition Fe₂₀Cr₄₀Ni₄₀O_x.⁴ After coating the Fe₂O₃-TiO₂ nanocomposite photoanode with these metal oxides, a favorable cathodic shift was measured presumably thanks to better water oxidation kinetics. At 1.03 V a photocurrent of 1.20 mA/cm² is obtained under AM 1.5 G simulated solar light, an almost two-fold increase compared to the Fe₂O₃-TiO₂ film. Further characterization methods addressing oxygen measurements and electronic structure are in progress.

[1] D. Monllor-Satoca et al., *Energy Environ. Sci.* **8**, 3242 (2015); [2] T. Ruoko et al., *J. Phys. Chem. Lett.* **6**, 2859 (2015); [3] R. D. L. Smith et al., *J. Am. Chem. Soc.* **135**, 11580 (2013); [4] J. B. Gerken et al., *Energy Environ. Sci.* **7**, 2376 (2014)

51 Synthesis of Microporous Nitrogen-Containing Polymer Nanoparticles with Homogeneous Noble Metals Incorporation for Catalysis

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Polymers are known for their low costs of production and their ease of handling. Thanks to the broad choice of monomers, it is facile to target a material with a specific composition. Based on this principle, this contribution is focused on nitrogen-containing polymers, for which the presence of active sites enables the synthesis of many different kinds of materials with specific applications, like adsorption, catalysis etc.

Nanoparticles of polyacrylonitrile, a polymer with repeating cyanide group, have been produced by emulsion polymerization. This polymer, when heat treated under specific conditions, can form micropores inside the polymer nanoparticle [1]. When considering this material as support for catalysts, an incorporation of the metal precursor during the synthesis and prior to heat treatment was considered [2]. The embedding of the metal into the polymeric structure is expected to prevent or at least hinder the sintering of active species during the final application as well as to achieve very high metal loadings within the nanoparticles. In addition, the heat treatment will create the necessary porosity and provide a facile access to the active sites for catalytic applications. As shown in Fig., a Platinum-based precursor was homogeneously incorporated inside the nanoparticles.

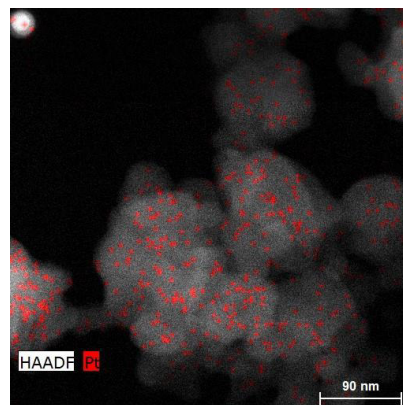


Fig. TEM EDX of Pt (M ab lines, enhanced) inside polyacrylonitrile nanoparticles.

[1] M. Rahaman et al., *Polym. Deg. Stab.* **92**, 1421 (2007); [2] Y. Yang et al., *J. Appl. Polym. Sci.*, **132**, 41933 (2015)

52 Gold-Catalyzed Formic Acid Decomposition for Application in the Selective Catalytic Reduction Process

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Urea is widely used as the ammonia storage compound for selective catalytic reduction (SCR) of nitrogen oxides in automobiles. However, the observable problems with urea have fostered immense interests in replacing this compound with alternative ammonia precursors, such as concentrated guanidinium formate, ammonium formate (AmFo) and methanamide solutions, that are more thermally stable, freeze at lower temperatures, have higher ammonia storage capacities and decompose more selectively.^{1,2} AmFo is experimentally the simplest choice to study the activity and behaviour of catalysts for the decomposition of the aforementioned precursors under realistic conditions.³ We identified Au/TiO₂ as a uniquely selective catalyst that converts AmFo into CO₂ without oxidizing the co-evolved ammonia even under highly oxidizing conditions prevalent in the exhaust gases.⁴ Moreover, the presence of gas phase ammonia lead to enhanced CO₂ production.⁵ Such a promotional effect was transformed into a catalytic effect by incorporating a base metal oxide into the catalyst.⁶ In-depth mechanistic investigations employing kinetic and spectroscopic measurements revealed that an oxidative dehydrogenation pathways proceeds under SCR-relevant conditions, which is markedly different from stoichiometric formic acid dehydrogenation that is commonly reported in literature.

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53 Atomically Dispersed Pd on TiO₂ by One-Step Flame Synthesis for NO Removal

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Reducing the particle size of noble metals on ceramic supports can maximize noble metal performance and minimize its use. Here Pd clusters onto nanostructured TiO₂ particles are prepared in one step by scalable flame aerosol technology while controlling the Pd cluster size from a few nanometers to that of single atoms. Annealing such materials at appropriate temperatures leads to solar photocatalytic NO_x removal in a standard ISO reactor up to 10 times faster than that of commercial TiO₂ (P25, Evonik). Such superior performance can be attained by only 0.1 wt% Pd loading on TiO₂. Annealing these flame-made powders in air up to 600 °C decreases the amorphous TiO₂ fraction and increases its crystal and particle sizes as observed by X-ray diffraction (XRD) and N₂ adsorption. The growth of single Pd atoms to Pd clusters on TiO₂ prepared at different Pd loading and annealing conditions was investigated by scanning transmission electron microscopy (STEM) and XRD. The single Pd atoms and clusters on TiO₂ are stable up to, at least, 600 °C for 2 hours in air but at 800 °C they grow into PdO nanoparticles whose fraction is comparable with the nominal Pd loading. So most of Pd atoms are on the TiO₂ surface where at 800 °C they diffuse and coalesce. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) reveals NO adsorption on single, double, 3- and 4-fold coordinated Pd atoms depending on their synthesis and annealing conditions. The peak intensity of NO adsorption sites involving multiple Pd atoms is substantially lower in TiO₂ containing 0.1 wt% than 1 wt% Pd but that intensity from single Pd atoms is comparable. This indicates the dominance of isolated Pd atoms compared to clusters in Pd/TiO₂ containing 0.1 wt% Pd that match or exceed the photocatalytic NO_x removal of Pd/TiO₂ of higher Pd contents.

54 Rapid Electrochemical Synthesis of Highly Porous CuO Foams Coated by ALD-Grown Al₂O₃ Films for Chemical Looping Combustion

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55 Rapid Aerosol Deposition of Thin, Flexible and Conductive Ag-Polymer Films

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Thin, flexible and conductive films are an essential component in many modern electronics which demand small size, light weight and high shape-conformability. These properties are frequently obtained by coating metals in intricate shapes onto polymeric substrates or combining conductive filler nanoparticles with polymers. Unfortunately not all proposed preparation methods are suitable for large scale fabrication. Inevitably, this has been leading researchers to evaluate roll-to-roll alternative such as inkjet printing and stamping. In this work, the flame synthesis of silver nanoparticles^[1] and their facile incorporation into polymers^[2] is presented for conductive silver-polymer nanocomposite films^[1,3]. Silver aerosol growth was shown to occur above the flame up to about 10 nm^[1]. Much larger nanosilver was obtained when directly depositing the aerosols onto polymer-coated substrates due to rapid coalescence of the incoming nanoparticles with the substrate bound ones^[1,3]. Sinter-necks form between the growing nanosilver leading to a percolating, and therefore conductive, nanoparticle network. The formation of this network in dependence on silver loading can be tracked by determining the sheet resistance by conventional four-point measurements. Here, a more precise *in situ* resistance measurement^[1] is proposed for determining this threshold, which even circumvents the fracturing of fragile sinternecks. *In situ* resistance measurements, furthermore, revealed a polymer substrate dependent formation of conductive nanosilver films. This detail becomes especially important for the rapid preparation of sub-micrometer thick films which retain their high electrical conductivity even during hundreds of bending cycles^[3]

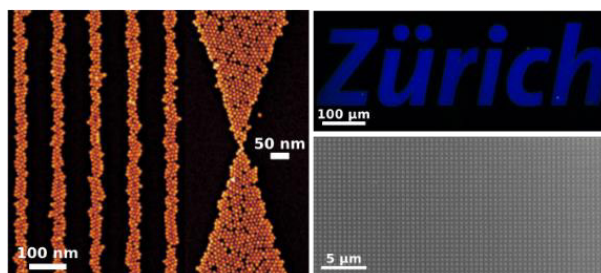
- [1] C.O. Blattmann et al., *Appl. Surf. Sci.* **371**, 329 (2016); [2] G.A. Sotiriou et al., *Adv. Funct. Mater.* **23**, 34 (2013); [3] C.O. Blattmann et al., *Nanotechnology* **26**, 125601 (2015)

56 Resist-Free Nanoparticle Patterning by Electron-Beam Exposure

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The development of nanoparticle-based electronics and plasmonics would benefit from a reliable and facile fabrication of nanoparticle structures. Direct electron-beam exposure is a simple method to produce patterns of nanoparticles from monolayers. Alkanethiol ligands attached to nanoparticles are transformed to an amorphous carbonaceous matrix linking particles to each other. A solvent can remove unexposed nanoparticles similar to a negative tone resist. So far, residual nanoparticles in unexposed areas and secondary particle layers on top of patterns have limited the potential for practical applications. Here, we introduce an emulsion-based development process to exploit the full potential of direct electron-beam patterning of nanoparticle monolayers on a Si/SiO₂ substrate. The formation of secondary nanoparticle layers is avoided by introducing the substrate first into water before adding an emulsion of tetra-hydrofuran (THF) and ammonium hydroxide. Development in a solvent alone leaves residual nanoparticles on the surface. Although unexposed nanoparticles can be dispersed in solvents like THF or toluene, they do not detach from the SiO₂ surface effectively. To this end, we add ammonium hydroxide, which is known to clean SiO₂ from residual particles. Starting with monolayers of 10-nm gold particles, we fabricated 25 nm wide line patterns and photonic structures larger than 700 μm.



57 Robust Decision Taking in Process Development with Multiple Objectives and Multiple Decision Variables

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The development of a process for the production of a product with several target characteristics is usually quite complicated. Independent of the field of application, such process development has to go through several iterations, where the variability from the target characteristics is constantly decreased so that eventually a product quality within the requested specification limits as well as an acceptable product quantity is achieved. In many industries, such limits can be defined very stringent by the regulatory authorities and can apply to a large number of product characteristics. In order to proceed efficiently, the process development team has to carefully plan the experiments to test for process conditions capable of ensuring the desired target characteristics as well as to correctly make decisions based on the generated results. In the presence of multiple process parameters (decision variables), multiple product-related objectives and a limited capacity for experiments this task is very complex.

This work presents a novel, generally applicable methodology based on Principal Component Analysis (PCA) and Decision Trees (DTs). Thereby, robustness is achieved through cross-validation of each step. It is applied to a case study from the pharmaceutical industry for the selection of cell line and media candidates as well as media supplements in the screening stage of the process development for a biosimilar (generic) therapeutic molecule. It is based on several hundred designed high-throughput cell culture experiments on 12 decision variables for 11 correlated product quality characteristics. The deduced selection criteria of the approach are then successfully validated on an external validation data set and are applied to experimental results from larger scales to show the potential of this approach for sequential process scale-up. Moreover, the results are compared to the ones obtained with a commercial tool revealing similarities and important advantages of the novel methodology.

58 Flowability Improvement of Powders Using Atmospheric Pressure Dielectric Barrier Discharge Plasma

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Powder is the predominant product form in industry. Due to cohesive forces between single powder particles, transportation and dosing of fine powder is challenging. To increase powder flowability, nanoparticles can be attached to the powder surface. They act as spacers and reduce van-der-Waals forces between powder particles by increasing the powder particle distance. Nanoparticles can be admixed in a time-consuming batch process. At LTR, we proposed the continuous production of silica nanoparticles and direct treatment of powder in a low temperature, low pressure argon glow discharge plasma using a silicon containing precursor [2]. This process only takes a fraction of a second and can increase flowability to the free-flowing regime. Low pressure processes however are very energy-intensive and vacuum equipment is too expensive for industrial application. Therefore, transfer to atmospheric pressure is necessary. To measure dissociation of different monomers in atmospheric pressure plasma and its afterglow, thin films were deposited on Si wafers using an argon/oxygen plasma with admixture of Hexamethyldisiloxane (HMDSO), Tetraethylorthosilicate (TEOS) or Tetramethylsilane (TMS). Monomers were either injected directly into plasma or in the afterglow region. Films were analyzed using white light interferometry (WLI) and ATR-FTIR to measure film thickness and film composition, respectively. Results show that admixture of 0.05% of oxygen yields highest deposition rates and therefore highest dissociation capability of the used plasma. TEOS and HMDSO show similar deposition rates, TMS deposition rates are significantly lower. TEOS and HMDSO deposition rates are comparable when monomer is injected into afterglow or plasma. Therefore, powder treatment in the afterglow of an atmospheric plasma is feasible using HMDSO or TEOS. Currently, optimal parameters for nanoparticle production in afterglow are investigated and the dielectric barrier design is adjusted for high throughput powder treatment.

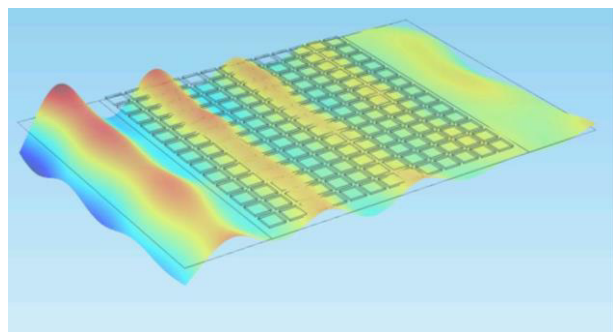
[1] J. Yang et al., *Powder Technology* **158**, 1 (2005); [2] C. Roth et al., *Plasma Processes and Polymers* **9**, 2 (2012)

59 2D Hybrid Dispersive Media with Controllable Wave Propagation

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In this paper, we report on the wave transmission characteristics of a hybrid two dimensional (2D) medium. The hybrid characteristic is the result of the coupling between a 2D mechanical waveguide in the form of an elastic plate, supporting the propagation of transverse waves, and a discrete network of interconnected electrical transmission lines, consisting of a series of inductors connected to ground through capacitors. The capacitors correspond to a periodic array of piezoelectric patches that are bonded to the plate coupling the two waveguides. The coupling leads to a hybrid medium that is characterized by a coincidence condition for the frequency/wavenumber value corresponding to the intersection of the branches of the two waveguides. In the frequency range centered at coincidence, the hybrid medium features strong attenuation of wave motion as a result of the energy transfer towards the electrical network. The distinct shape of the dispersion curves suggests that energy transfer is due to weak coupling eigenvalue phenomena. Moreover, the 2D system offers increased design parameters in both the electrical and mechanical domains. The additional mechanical degrees of freedom were investigated by calculating the dispersion relations for the piezoelectric elements arranged following the five 2D Bravais lattices. In the lattices, the electrical network connections also followed the pattern of the piezoelectric element layout. In addition, the ability to conveniently tune the dispersion properties of the interconnected network of electrical transmission lines was exploited by studying the dispersion a square geometry lattice with diatomic inductances.



The diatomic inductances allow for anisotropic wave propagation by means of directional tuning of the electrical network. Further insight was given to the dispersion curves of the configuration which yielded the greatest coupling between eigenvalue phenomena over a broad frequency range, by investigating the transmittance on a finite plate with 13 by 13 piezoelectric elements. The medium consisting of mechanical, piezoelectric, and analog electronic elements can be easily interfaced to digital devices to offer a novel approach to smart materials.

60 Sintering Rate and Crystal Structure of Gold Nanoparticles by Molecular Dynamics

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Gold nanoparticles find a score of applications in catalysis, plasmonic biosensing, target-specific drug-delivery, nanolithography and ion detection. However, their size, shape composition and crystal structure strongly affect final product properties and eventually plasmonic, optical, photothermal or catalytic performance, especially below 10 nm (in the order of Au electron mean free path) that particles' behavior differ both from the bulk metal and the molecular compounds. For example, small nanoparticles are more attractive as catalysts than larger particles due to their increased activity and selectivity.

Here, MD simulations are used to investigate the sintering mechanism and crystallinity dynamics of gold nanoparticles of various sizes and temperatures as they provide useful physical insight in understanding phenomena such as sintering and crystal structure changes in atomistic scale. The trajectories of the surface and bulk atoms reveal that sintering primarily takes place by surface diffusion at most conditions due to the increased mobility of surface atoms, while grain boundary diffusion mostly occurs (along with surface diffusion) in large particles and high temperatures at sufficiently long times. The stage of crystallinity is theoretically investigated by the deviation of each gold atom from a perfect face cubic centered crystal. This deviation is quantified by the so-called Steinhardt parameters which are measures of the local and extended orientational symmetries of the particle. During adhesion, particles reveal increased degree of distortion compared to later stages of sintering, regardless of particle size and sintering temperature, while they form grains of different size and orientation. Large particles (e.g. 4 nm in diameter) form twin boundaries, consistent with experiments of Au nanoparticles coalescing by electron beam irradiation. Coalescing particles of diverse initial crystallinity result in significantly different polycrystalline materials (multiple twin boundaries) that form by different sintering rates, even though formation of completely amorphous particles is observed before recrystallization takes place.

61 Confocal Reference-Free Traction Force Microscopy

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The mechanical wiring between cells and their surroundings is fundamental to the regulation of complex biological processes during tissue development, repair or pathology. Traction Force Microscopy (TFM) enables determination of the actuating forces. Despite progress, important limitations with intrusion effects in low resolution 2D pillar-based methods or disruptive intermediate steps of cell removal and substrate relaxation in high resolution continuum TFM methods need to be overcome. Here we introduce a novel method allowing a one-shot (live) acquisition of continuous, 3D force fields with high sensitivity. The method is based on electrohydrodynamic nanodrip-printing of quantum dots into confocal monocrystalline arrays, rendering individually identifiable point light sources on compliant substrates. We demonstrate the unprecedented, undisrupted reference-free acquisition and quantification of high-resolution force fields, and the simultaneous capability of this method to correlatively overlap traction forces with spatial localization of proteins, for which no reliable live-cell reporter is available.

62 Nascent Soot Formation by Agglomeration and Surface Growth

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Nascent soot particles of mobility size 1 – 10 nm are the building blocks of diesel soot, a major environmental pollutant, but also carbon black, a valuable commodity material used in reinforcing tires and other industrial rubber products. Major concerns have been raised about nascent soot, since microscopy and mass-mobility measurements have proved the existence of ultrafine aggregates. So, their impact on climate, health and nano-materials manufacturing needs to be determined accurately.

Here, Discrete Element Model (DEM) simulations are used to investigate the dynamics of nascent soot particle growth after nucleation accounting for simultaneous surface growth and agglomeration in the absence of soot oxidation. Nascent soot growth by agglomeration with or without acetylene molecule reaction (pyrolysis) is compared to that by full coalescence. Neglecting the non-spherical or fractal-like nature of soot underestimates its aggregate polydispersity up to 40 %. The DEM-obtained size distributions of soot growing by agglomeration with surface growth are in good agreement with microscopy and mass-mobility measurements of a benchmark ethylene flame, indicating that surface growth narrows down soot size distributions at low heights above the burner, consistent with literature. The evolution of nascent soot structure from spheres to aggregates quantified by the mass fractal dimension and mass-mobility exponent is also in excellent agreement with experiments. Surface growth bonds chemically the constituent primary particles of aggregates. The effect of soot volume fraction on nascent soot morphology is elucidated. Based on the aggregate projected area, a scaling law is derived for the number and size of the nascent soot primary particles from mass-mobility measurements.

63 Bicomponent Fibers for Thermoplastic Composites: Concept and Manufacture

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We propose an alternative concept for hybrid intermediate materials used in high volume production of thermoplastic composites by coating individual glass filaments with a polymer sheath. Such bicomponent fibers provide a full wet-out while retaining the handling possibilities of fiber rovings. Dip-coating in-line with the glass fiber spinning process is suggested as a potential fabrication route and the feasibility of this method is assessed through theoretical considerations. Finally, a proof of concept for dip coating single filaments in dilute polymer solutions is given.

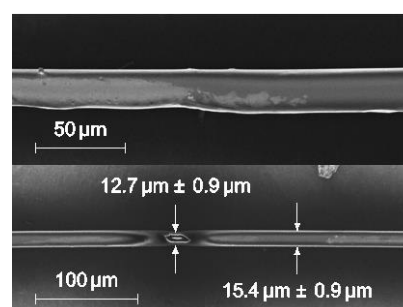


Fig. 1. Micrograph of a bicomponent fiber (top) and burnt polymer sheath revealing the glass core (bottom).

64 Predicting the Fractal-Like Structure of SiO₂ Nanoparticles through Molecular Dynamics Simulations Using the Potential of Mean Force

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We will present a multi-scale simulation approach that allows the study of the fractal-like structure of nanoparticles in the gas phase and the dependence of the corresponding fractal exponents on the Knudsen number directly from the chemical structure of the primary particles. Our methodology entails three main steps: (1) calculation of the effective potential (potential of mean force) between two primary particles using a very accurate atomistic force-field, (2) molecular dynamics (MD) simulations with the effective potential, and (3) analysis of the accumulated trajectory to obtain the dependence of the radius of gyration of the agglomerates formed in the course of the MD simulation on the number of primary particles per agglomerate. The effective potential is computed as the orientational configurational average of the potential energy between two primary particles held at a fixed separation, and it is found to be strong function of the nanoparticle diameter. The subsequent MD simulations are executed in the NVT statistical ensemble using a very small time step (equal to 3 fs) but allow us to reach simulation times on the order of several decades of microseconds since every primary particle is

treated as a single atomistic unit. We have successfully applied our approach to agglomerates formed by amorphous SiO₂ nanoparticles of different diameter, at ambient conditions. We will present results for the asymptotic fractal exponents in the free molecular and continuum regime (also their “running” with the Knudsen number) and we will thoroughly compare them with analogous results obtained through calculations based on the discrete element modeling method [1]. To the best of our knowledge this is the first simulation effort to predict the fractal exponents of agglomerated nanoparticles directly from the knowledge of the chemical constitution of the constituent primary particles.

[1] E. Goudeli et al., *Langmuir* **31**, 1320 (2015)

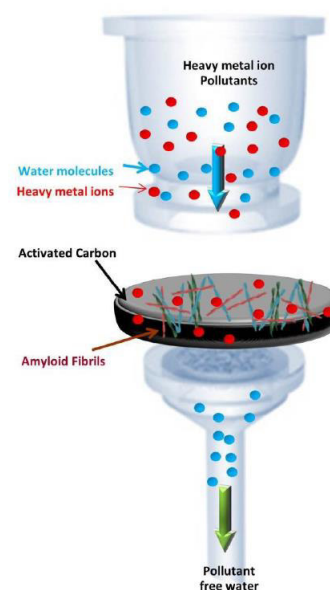
65 Hybrid Membranes: Snatch Contaminants from Water and Strike Gold

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Industrial development has dramatically increased the levels of environmental pollutants such as heavy metal ions, cyanides and nuclear waste, but current technologies for water purification are expensive and ion specific. We have invented inexpensive hybrid membranes made from protein amyloid fibrils and activated carbon that can be used to remove heavy metal ions and radioactive waste from water with unprecedented efficiencies, even when filtering several ions simultaneously. The same membranes can be used to recycle valuable heavy metal contaminants by thermally reducing and converting them into elemental metal nanoparticles and films, turning a pressing global problem into a unique opportunity.

S. Bolisetty et al., *Nature Nanotechnology* **11**, 365 (2016)



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