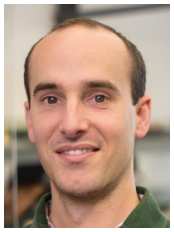
C'NANO 2018
THE NANOSCIENCE MEETING
TOULON December, 11, 12 and 13
Palais des Congrès Neptune
In partnership with: Club nanoMétrologie LNE RENATECH



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Biography

Prof. Julien Bachmann studied chemistry at the University of Lausanne, Switzerland, and obtained his doctoral degree in molecular inorganic chemistry from the Massachusetts Institute of Technology in the USA in 2006. He obtained a Humboldt Fellowship to learn the chemistry and physics of solids at the Max Planck Institute of Microstructure Physics in Germany, then moved to the University of Hamburg, where he obtained an Assistant Professor position in physics and chemistry in 2009 to start his independent work on energy-converting nanostructured interfaces. Prof. Bachmann was appointed as an Associate Professor of Inorganic Chemistry at the Friedrich-Alexander University of Erlangen-Nürnberg in 2012. In 2017, he was promoted to the Full Professor status, and he now leads the Chair 'Chemistry of Thin Film Materials' at FAU. Macroporous materials, thin coating methods, electrocatalysis, photoelectrochemistry and photovoltaics belong to the main areas of research in the Bachmann group, supported among others by an ERC Consolidator Grant.

ATOMIC LAYER DEPOSITION: FROM METHOD DEVELOPMENT TO GEOMETRICALLY ENGINEERED NANOMATERIALS AND FUNCTIONAL INTERFACES - THEN VICE VERSA

The ability to convert solar energy and store it in chemical form in benign conditions at low cost will imply the exclusive use of inexpensive, abundant materials instead of the most advanced catalysts and semiconductors. One strategy to achieve this goal consists in accurately controlling the interface's microscopic geometry. 'Anodic' nanoporous templates and atomic layer deposition (ALD, a gas-solid coating technique controlled by surface chemistry) yield structured electrode surfaces with a tunable geometry of ordered pores. Their diameter and length are set accurately and varied systematically.

Transport-limited transformations remain unaffected by changes in their length, whereas electric current densities observed for slow processes limited by electron exchange at the interface increase linearly with the pore length. These effects are exploited to optimize the mass activity of noble metal electrocatalysts for the water oxidation reaction, to increase the electrolytic turnover at the surfaces of abundant transition metal oxide surfaces by several orders of magnitude, and to achieve even further gains by combining several layers of distinct materials.

In the photovoltaics field, ALD can be exploited to generate several layers of the stack: electron conductor, light absorber, as well as recombination barrier. Here, the ALD method's ability to yield highly pure films of extremely well controlled thickness is of crucial importance. It enables the experimentalist to optimize each layer with an accuracy better than 1 nm. However, the unavailability of traditional ALD reactions for a number of interesting photovoltaic materials spurs research into original thin film coating techniques. ALD from dissolved precursors is one promising novel development which gives access to materials families completely or mostly foreign to ALD, such as polymeric and ionic solids.

Keywords: thin films, atomic layer deposition, photovoltaics, electrocatalysis

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Biography

Bernhard Urbaszek is a CNRS Research Director at Laboratory of Physics and Chemistry of Nano-objects (LPCNO). His research topics include:

- 2D van der Waals materials
- Spin and valley physics
- Optical spectroscopy and optoelectronics
- Quantum dots
- Nuclear spin dynamics

He did his PhD and postdoc at Heriot-Watt University, Edinburgh before moving to Toulouse in 2003. He was first working as a Lecturer at INSA Toulouse teaching Solid State Physics, Optoelectronics and Quantum Mechanics before joining CNRS in 2008.

Optical and Spin-valley properties of atomically thin semiconductors

The family of semiconducting transition metal dichalcogenides (TMDs) is an especially promising platform for fundamental studies of two-dimensional (2D) systems, with potential applications in optoelectronics and spintronics. When thinned down to one atomic monolayer, optical transitions at the direct optical band gap lead to highly efficient light-matter coupling, with 20 % light absorption per monolayer. A crystal lattice with broken inversion symmetry combined with strong spin-orbit interactions leads to a unique combination of the spin and valley degrees of freedom for electrons. In addition, the 2D character of the monolayers and weak dielectric screening from the environment yield a significant enhancement of the Coulomb interaction. The resulting formation of bound electron-hole pairs, or excitons, dominates the optical and spin properties of the material. Optical manipulation of valley polarization memory for excitons and resident carriers is described and future challenges are laid out.

Keywords:

11, 12 & 13 septembre
Session (nanophotonics)
Keywords: nanoparticles, plasmonics, microsensor, mechanochromics, colloids

MIcrosensing with plasmonic-based mechanochromic microparticles

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Many natural processes start with an alteration of their immediate environment at the microscopic level. Monitoring these local alterations require the fabrication of smart microsensors that are cost-effective, easy to disperse, sense local changes, and have the ability to translate this change into a large, unambiguous signaling output. One class of colloids has been developed in recent years, based on the combined assembly of molecular dyes absorbed, covalently attached to a polymeric backbone or encapsulated. Though this type of sensors has proved very efficient, it requires complex chemistry with dyes attached to the polymeric backbone or a perfect control of the leaking when dyes are encapsulated. Here, we show how the combined assembly of optically active nanoparticles and stimuli-responsive polymeric colloids paves the way for an alternative class of microsensors able to transform chemical potentials or external forces into a large and easily detectable optical signal.

Congrès 2018, Toulon

11, 12 & 13 septembre
Session (Nanochemistry, Synthesis and Assembly or Advanced Functional Materials)
Keywords: 'Self-Assembly, Films, Metal-Organic Frameworks, Photonics, Sensors'

Self-Assembling Cracks in Nanoparticles Films:

How to Turn a Drawback into Functionalities

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Patterning colloidal films could potentially open perspectives for their utilization in fields ranging from electronics, photonics, microfluidics or dew-harvesting (1). For example, in the field of photonics, the combination between the unique properties of nanomaterials and of 2D periodic structures could allow the fabrication of a new generation of performing optical devices and sensors.(2)
Formation of cracks in colloidal films is generally considered as major drawback. However, in controlled conditions the drying of colloidal droplets results in the formation of parallel periodic cracks oriented by the evaporation front-line (3).
Inspired by the formation of cracks in mud, we demonstrate that crack formation can be controlled through a novel methodology called "Evaporation-directed Crack Self-Assembly". (4) As case of study, Metal-Organic Framework colloidal films (sub-50 nm MIL 101 or ZIF-8) were crack-patterned during dip-coating deposition by orienting the crack propagation with the evaporation front. We show that arrays of periodic cracks diffract lights and can be used as photonic platform. We also propose a new concept of "on-demand" optical sensors, based on MOF diffraction gratings, with outstanding sensitivity, easily adjustable as function of the desired detection range.(4)
In addition, this "bottom-up" method was further extended to other nanomaterials (polymers,oxyde, fluoride, plasmonic particles…) for their direct integration into patterned devices without the limitations of the conventional lithographic techniques.

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11, 12 & 13 septembre
Session (Nano-optics)
Keywords: 'Single semiconductor nanoparticles, fluorescence microscopy'

Analysis of the fluorescence dipole structure for single CdSe/CdS nanoplatelets

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Fluorescent semiconductor nanostructures are presently used or studied for lighting, display or photovoltaic applications, which requires in-depth understanding of their photophysical properties. The fluorescence radiation can sometimes be described as a single linear dipole. However for many emitters two or more degenerate states contribute to the fluorescence and the radiation must then be described by an incoherent sum of dipoles. This dipole structure of an emitter can be assessed by polarimetric analysis, however this is complicated by the lack of knowledge on the emitter's orientation [1].

We present here an analysis of the dipole structure of various CdSe/CdS nanoplatelets samples of square, rectangular and cubic geometries, by a method combining polarization and radiation pattern (emission angular distribution) analyses. For each sample, the emission of single particles could be described by a sum of dipoles reflecting both the distribution of the radiating electron-hole pair and the dielectric shape of the nanoparticle [2,3].

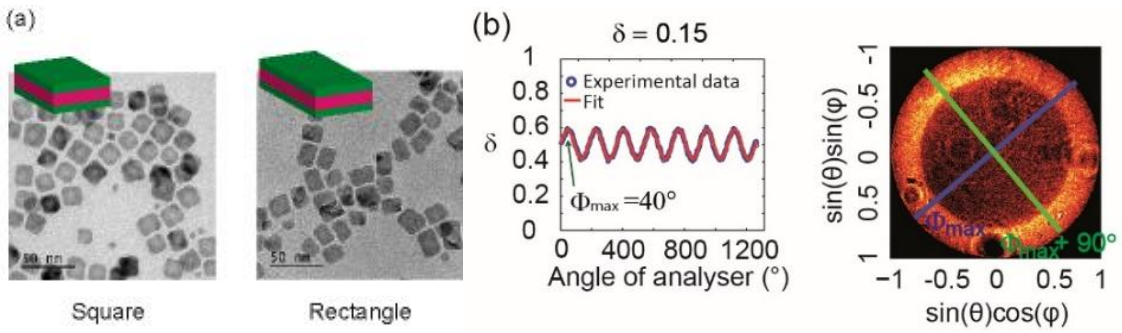

Figure 1 : (a) TEM images of the square and rectangle nanoplatelets; b) Measured emission polarization curve and radiation pattern for a rectangular nanoplatelet.

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11, 12 & 13 septembre
Session : Advanced functional materials
Keywords: sensors, aluminum-doped zinc oxide nanostructures, ink – jet printing

Inkjet-printed aluminum-doped zinc oxide nanostructures

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Abstract

Our studies were focused on the inkjet-printing of aluminum-doped zinc oxide (AZO) nanostructures. In our case, AZO platelets and isotropic nanoparticles were synthesized by aqueous coprecipitation at the GREMAN laboratory. These structures turn out to be very promising candidates for sensor applications due to its good transparency, conductivity and non-toxicity. Then, the preparation of the solvent-based ink was performed at the ICMN laboratory with the control of the viscosity, ink stability and nanoparticles dispersion. Fabrication processes of first electro-chemical sensor's prototypes were studied at the GREMI laboratory using a Dimatix system based on tiny MEMS nozzles to print AZO active thin film materials onto substrates. This allows low manufacturing costs and surface shapes flexibility. First tests of molecule detection were performed using an electrochemical sensor designed as a proof-of-concept.

11, 12 & 13 septembre
Session Advanced nanomaterials for photonics
Keywords: Optical fibers, drawing, Rayleigh-Plateau, break-up

Drawing optical fibers: a top-down approach to shape oxide nanoparticles

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Optical fibers form the basis for a wide range of applications that have grown considerably in technological impact recently, such as telecommunications, sensors, and lasers. These applications rely on the remarkable qualities of silica glass; particularly its significant mechanical and chemical stability, high optical damage threshold, low cost, and very high transparency. However, silica also possesses certain characteristics that are detrimental for luminescence ions including low rare-earth dopant solubility and relatively high vibrational energies. To overcome these issues, the incorporation of rare-earth ions into oxide nanoparticles, which are then doped into the silica, is investigated to tailor the spectroscopic properties through the control of their local chemical environment around the dopant. Such optical fibers are elaborated by a high temperature fiber drawing (2000°C) of nanoparticles-doped optical preforms. The drawing step is usually assumed to be a homothetic transformation of the preform. However, at this stage, the glass is heated to a temperature at which it softens and then flows. In this presentation, we highlight the elongation and even break up of oxide nanoparticles during the draw process. In particular, we will focus on the comparison between experimental results (Tomography-based (FIB/SEM) and X-ray nanotomography Multiscale imagery) and numerical simulations in Molecular Dynamics. Such modifications are explained by Rayleigh-Plateau instabilities and the competition between viscous forces and surface tension. These observations allow us to envision a new top-down strategy, the use of these phenomena to tailor optical properties through the control of the size and shape of nanoparticles during the draw step.

Session : Advanced nanomaterials for photonics or Nano-optics, nanophonics and plasmonics
Keywords: laser-induced mechanisms, metallic nanoparticle growth, non-linear feedback mechanisms

Increased heating of metallic nanoparticles for lower deposited light energy: measurement and explanation of a counter-intuitive behavior

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Irreversible dynamic processes driven by non-linear feedback mechanisms play an important role in many natural and artificial systems. Besides their fundamental interest, such processes have the remarkable ability to naturally enable the emergence of new properties for materials that are hardly achievable or unachievable by other means. Here, we focus on processes triggered by light–matter interactions, during the scanning of a focused cw visible laser beam on a plasmonic nanocomposite film. The latter is made of a TiO_2 matrix and contains Ag nanoparticles that can shrink or grow upon laser excitation. The time evolution of Ag nanoparticles during the laser passage is shown to be intimately related to the temperature rise measured in the laser spot. We demonstrate, by in situ measurements, a counter-intuitive behavior of such a film that is: the higher the scanning speed the higher the temperature rise. The latter is measured using either Raman microspectroscopy or cross-polarization imaging. We also propose a model and simulation results to explain such a behavior. This model highlights the competitive contribution of five physico-chemical mechanisms that are the photochemical release of silver ions after ionization of nanoparticles, the reduction of silver ions, the ripening of nanoparticles, their coalescence and heat diffusion. Simulations evidence how the tunable triggering of positive feedbacks, which introduce strong non-linearities, determines the system thermal evolution and the nanoparticle growth. Such laser writing processes are applied to the generation of plasmonic colors and to innovative color image mutliplexing.

Congrès 2018, Toulon

11, 12 & 13 decembre
Session: Nanophotonics
Keywords: 'Mid-IR Nanoantennas', 'SEIRA', 'Gas sensing', 'Hybrid materials' ,'Zeolites'

SEIRA detection of benzene at ppb levels mediated by resonant nanoantennas

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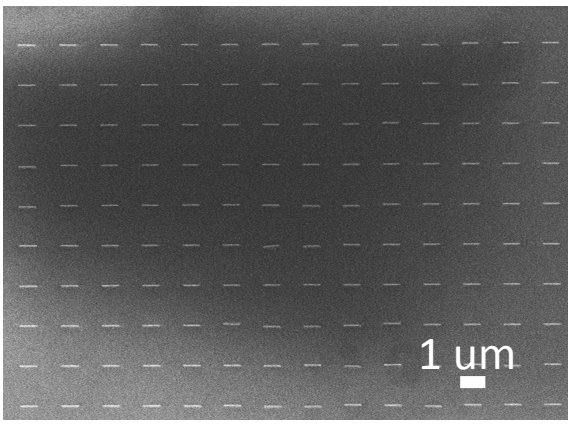
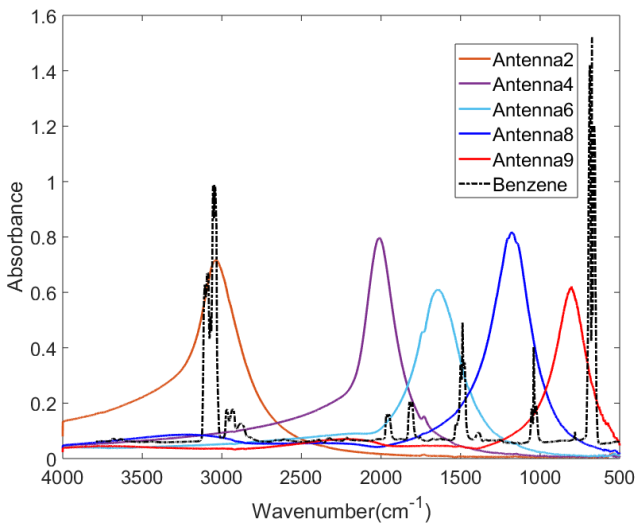
The detection of volatile organic compounds (VOC) at trace levels (ppb), such as **benzene**, is expected to have a role of increasing impact in the field of environmental monitoring for health related issues. Commercial portable low-cost sensors typically monitor changes (such as conductance) in a responsive material. These approaches can be very sensitive for a specific VOC target (ppb range), but they often lack of versatility and/or selectivity.
Spectroscopic techniques in the mid infrared (3-20 um) are able to detect the *unique* fingerprints of molecular transitions, but they are strongly limited by the extremely weak light-matter interaction (a^3/λ), thereby requiring long optical paths to boost the signal to noise ratio for applications where *ppb* levels of detection are required.
The use of **resonant nanoantennas** to boost the sensitivity (Surface Enhanced Infrared Absorption – **SEIRA**) has been so far limited to the detection of organic monolayers adsorbed on the antennas surface, where the field enhancement is the highest.
We will present a new approach, that enables to **extend** SEIRA to the detection of **gases**.
This is based on the combination of a *concentrating inorganic material*, such as zeolites to trap gas molecule and locally increase the concentration (***chemical enhancement***), with *phased array of resonant nanoantennas* to locally boost light-matter interaction (***photonic enhancement***).
Experimental data show that with this *hybrid system* an absorbance **enhancement >10^7** is obtained. This allows to detect benzene at concentrations as low as **10 ppb** in 1-2 minutes, and to discriminate it from other VOCs such as toluene.





A novel random connection principle for wire-based solar cells: $NiSi_x$ nanowires.

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Wire-based solar cells are composed of arrays of vertical, micron-diameter semiconductor p-n radial wires. Those microwires (μWs) are grown by the vapor-liquid-solid process. The usual way to connect one of the two electrodes, after the growth of the array, is to deposit a layer of indium-tin-oxide (ITO) on top of the μWs. However, shadowing effects during deposition induce a non-uniform thickness and an increase in the series resistance, which decreases the efficiency of the cell. Also, the surface of the μWs presents a high concentration of defects, that need be passivated with oxide or nitride films. Since these films are insulators, if they are deposited before the ITO, the devices tend to exhibit a high contact resistance, which affects again the efficiency.

We have recently introduced a connection principle where a random array of $NiSi_x$ nanowires (instead of ITO) connects Si-μWs[1]. We have used a planar geometry for the solar cell, with interdigitated electrodes and the active area of the cell was ~ 33% of the footprint of the device, yielding an efficiency of 4.5% only. In the present work, by modifying the size of the electrodes, we have increased the active surface area to ~ 55% of the footprint and obtained an efficiency of ~ 7%, which scales with the increase of the active surface area.

Details on the manufacturing process as well as the possible evolution towards a 3D structure will be presented and discussed at the workshop.

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11, 12 & 13 septembre
Session Nano-optics, nanophotonics and plasmonics
Keywords: nanoparticle self-assembly, nanowires, plasmonics, chirality, electronic transport

Anisotropic optical and electronic properties of oriented self-assembled thin films of 1-D metallic nanoparticles

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Recently there has been great interest in designing thin film materials that possess highly anisotropic properties. For this purpose, metal nanoparticles are particularly interesting due to their localized surface plasmon resonance and high conductivity, and significant progress has been made in the area of metallic nanowire and nanorods synthesis and device application in the past several years. The hierarchical organization of these nanoscale building blocks into functional assemblies and ultimately a useful system is still a challenge, and discovering new bottom-up methods to assemble one-dimensional nanomaterials into two- or three-dimensional structures with well-controlled location, orientation, and spacing across multiple length scales has attracted lots of attention, owing to the potential applications in electronic and optical devices.

In this talk, I will show how Grazing Incidence Spraying, a new assembly technique we have recently introduced, allows forming oriented thin films of anisotropic nano-objects over large areas with highly anisotropic optical and electrical properties [1-4]. The Layer-by-Layer assembly approach is used to build multilayer thin films of oriented gold nanorods and silver nanowires, paving the way for hybrid thin films with complex and tuneable architecture, e.g. for plasmonic chiral layers showing giant circular dichroism.

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