Self Assembly and Molecular Electronics

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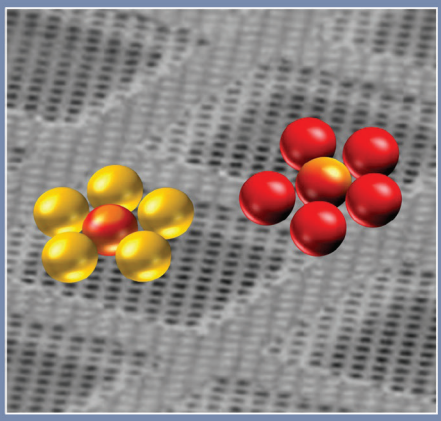

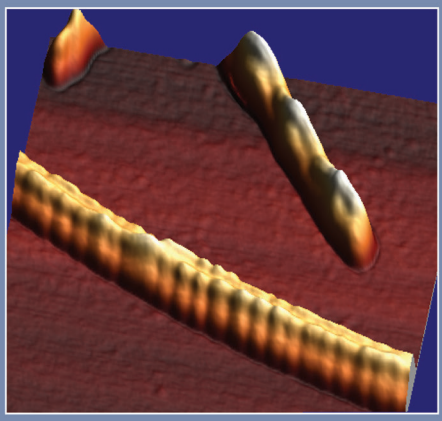

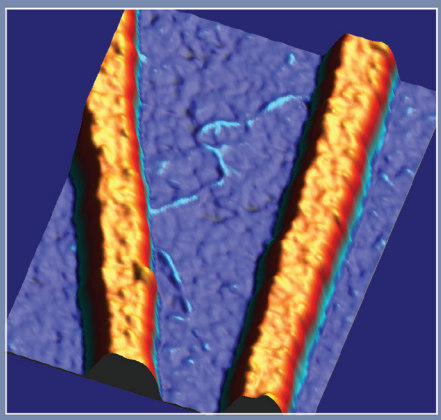

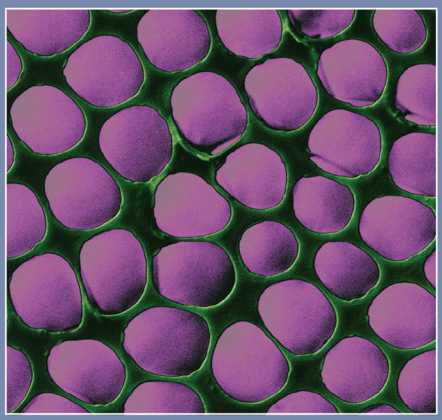

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Tel Aviv University, Israel

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Towards Single Electron Nanoelectronics Using Self-Assembled DNA-Structure

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11:00 – 11:20

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Scientific Research Institute of Physical-Chemical Medicine, Russia

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Chalmers University of Technology, Sweden

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Behabitu Tebikachew

Chalmers University of Technology, Sweden

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University of Jyväskylä, Finland

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Steffan Møller Sønderskov
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Jens Peter Froning
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Giorgia Brancolini

CNR Institute of Nanoscience, Italy

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Columbia University, the USA

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Elena Ferapontova
iNano, Aarhus University, Denmark

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Isabel Alvarez-Martos
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Dmitry Kazantsev
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University of Natural Resources and Life Sciences, Austria

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iNano, Aarhus University, Denmark

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Jonas Beermann
University of Southern Denmark, Denmark

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Niclas Solin

Linköping University, Sweden

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Dapeng Cao

Beijing University of Chemical Technology, China

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Laszlo Kekedy-Nagy

iNano, Aarhus University, Denmark

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Yury Lyubchenko

University of Nebraska Medical Centre, the USA

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Deby Fapyane
iNano, Aarhus University, Denmark

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Andrew Pike	Newcastle University, UK
Behabitu Tebikachew	Chalmers University of Technology, Sweden
Christian Bortolini	Arhus University, Denmark
Cristian Pablo Pennisi	Aalborg University, Denmark
Daojian Cheng	Beijing University of Chemical Technology, China
Dapeng Cao	Beijing University of Chemical Technology, China
Deby Fapyane	Aarhus University, Denmark
Dennis Achton Nielsen	Aalborg University, Denmark
Dmitry Kazantsev	Institute for Theoretical and Experimental Physics, Russia and NT-MDT Spectrum Instruments, Zelenograd, Russia
Dmitry Klinov	Scientific Research Institute of Physical-Chemical Medicine, Russia
Elena Ferapontova	Aarhus University, Denmark
Erik Reimhult	University of Natural Resources and Life Sciences, Austria
Francesca Risplendi	Politecnico di Torino, Italy
Giorgia Brancolini	Institute of Nanoscience (CNR-NANO S3), Modena, Italy
Gloria Saracino	Fondazione Casa Sollievo della Sofferenza IRCCS Opera San Pio da Pietralcina, Italy
Isabel Alvarez-Martos	Aarhus University, Denmark
J. Gómez-Herrero	Universidad Autónma de Madrid, Spain
Jens P. Froning	Palacký University Olomouc, Czech Republic
Johnas Eklöf	Chalmers University of Technology, Sweden
Jonas Beermann	University of Southern Denmark, Denmark
Jussi Toppari	University of Jyväskylä, Finland
Kasper Moth-Poulsen	Chalmers University of Technology, Gothenburg, Sweden
Kosti Tapio	University of Jyväskylä, Finland

Lasse Christiansen	Aalborg University, Denmark
László Kékedy-Nagy	Aarhus University, Denmark
Leonid Gurevich	Aalborg University, Denmark
Lingling Zhang	Aarhus University, Denmark
Masoud Baghernejad	University of Basel, Switzerland
Mathieu Linares	KTH Royal Institute of Technology, Sweden
Mingdong Dong	Aarhus University, Denmark
Mohtadin Hashemi	University of Nebraska Medical Center, United States
Morten Slyngborg	Aalborg University, Denmark
Niclas Solin	Linköping University, Sweden
Peter Fojan	Aalborg University, Denmark
Rafael Taborysky	Technical University of Denmark, Denmark
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Victoria Birkedal	Aarhus University, Denmark
Winnie Svendsen	Technical University of Denmark, Denmark
Yuri L. Lyubchenko	University of Nebraska Medical Center, United States

Abstracts

16/11/2016

09:05 – 09:45

DNA-Nanoparticle Wires

Alexander Kotlyar*, Gennady Eidelshtein and Benjamin Kempinski

Department of Biochemistry and Molecular Biology,
George S. Wise Faculty of life Sciences and The Center of Nanoscience and Nanotechnology, Tel Aviv University, Ramat Aviv,
Tel Aviv 69978, Israel
**E-mail: s2shak@post.tau.ac.il*

I am going to talk about novel DNA-based molecular nanowires composed of a linear double stranded (ds) lambda DNA and gold nanoparticles (GNPs). Other types of DNA, such as circular and linearized plasmids DNA or synthetic double stranded nucleic acid polymers can also be used. The first step of the wires production includes formation of conjugates between the DNA and small (1–2 nm in diameter) phosphine-coated gold nanoparticles. This reaction is taking place on a mica surface upon treatment of deposited DNA molecules with suspension of the nanoparticles at low (2–3) pH. Binding of the particles is specific with respect to DNA; almost no particles were found

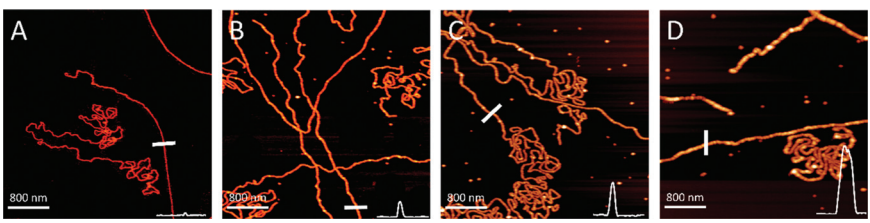

Figure 1 GNPs enlargement on the DNA template. Lambda DNA complexed with the GNPs (A) were treated with a mixture of 1 mM ascorbic acid and 20 (B) or 40 (C) and 100 μM (D) gold ions for 20 sec. The surface was then rinsed with double distilate water and dried by blowing nitrogen gas. Statistical height analysis of the AFM images performed on many molecules yields the average heights of: 1.5±0.2, 5.1±1, 10.2±2 and 25.4±4 nm for panels A, B C and D respectively.

in between the deposited DNA molecules (see Figure 1B). One can speculate that positively charged (at acidic pH) bases of the DNA attract negatively charged nanoparticles while the negatively charged mica repulses the particles. Thanks to the selectivity of the particles binding, we succeeded to produce the DNA-GNPs conjugates on the surface. The height of the conjugates is ∼1.5 nm which corresponds nicely with binding of ∼1 nm (in diameter) nanoparticles to the DNA (the height of the dsDNA measured by AFM is ∼0.5–0.6 nm).

The particles bound to the DNA can be enlarged. This can be done by treatment of the mica surface with a mixture of ascorbic acid and gold ions (see schematic drawing in Figure 2). The treatment yields relatively uniform molecules, which are thicker than the initial DNA-GNP conjugates. As seen in Figure 1, the height of the conjugates increased from 1.5 to approximately 5, 10 and 25 nm depending on concentration of gold ions in the enhancement solution (compare panel B with C and D). The height of the DNA-GNP conjugates therefore can be varied in a controlled manner. It is thus possible to control the diameter (which corresponds to the AFM-measured height) and the length (using different DNA molecules) of the fibers.

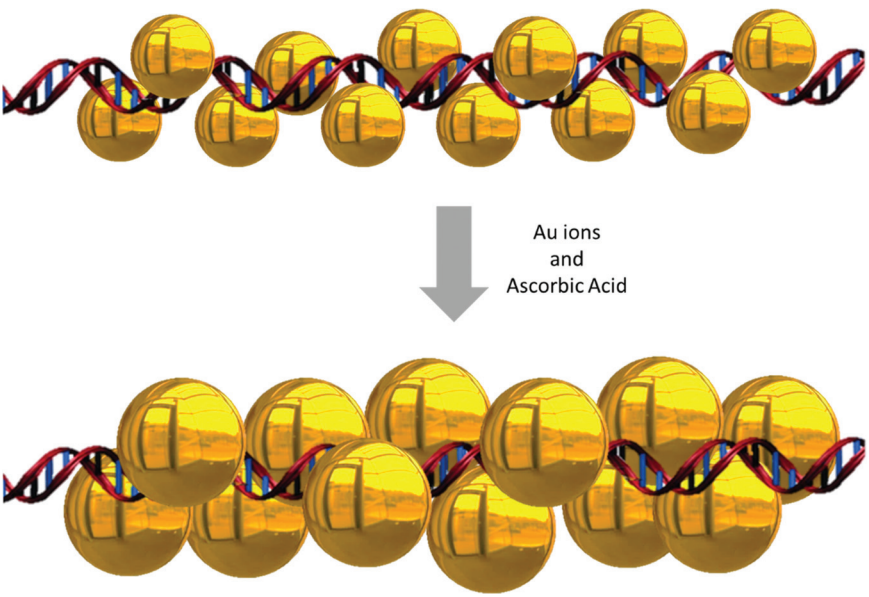

Figure 2 Schematic drawing of GNPs (gold-colored spheres) on a DNA template.

The results obtained recently in the laboratories of Prof. Danny Porath from Hebrew University of Jerusalem and Dr. Dmitry Klinov from Moscow Institute of Physical-Chemical Medicine demonstrates high conductivity of the DNA-GNP conjugates which makes them promising candidates for nanoelectronic applications.

09:45 – 10:25

Towards Self-Assembled Single-Molecule Electronic Devices

Kasper Moth-Poulsen

Department of Chemistry and Chemical Engineering,
Chalmers University of Technology, Gothenburg, Sweden
E-mail: kasper.moth-poulsen@chalmers.se

Recent years have seen progress in several areas regarding single molecule electronic devices. A number of interesting structure–property relationships have been observed, including vibronic effects, spin transitions, and molecular electronic interference known as quantum interference. Together, these observations highlight what the rich opportunities in molecular design might bring in terms of advanced device properties [1]. Pertinent challenges in the field of are related to development of high yield preparative procedures for fabrication of single molecule devices in a parallel and reproducible way. With this presentation we highlight our recent progress considering self-assembled formation of metal nanogaps incorporating single molecules for single molecule electronics applications. We discuss methods for the formation of the nanogaps as well as methods attempting to achieve single molecule functionality in each individual device [2]. Examples include fabrication of single molecule devices by in-situ growth of gold nanorods [3], formation of nanogaps via deterministic self-assembly of gold nanorods [4], single molecule transport studies under influence of force pulling [5], a method for self-assembly of nanoparticle heterodimers, allowing for monitoring thermodynamics of hydrogen absorption on single particles [6] designed molecules

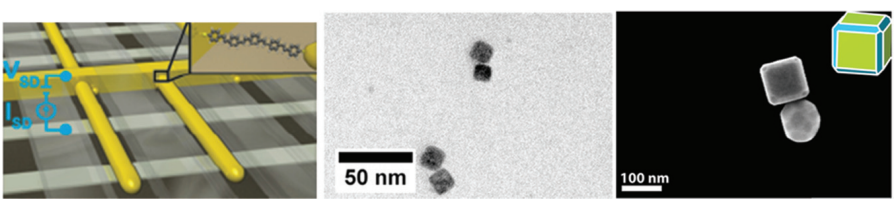

Figure 1 (left) self-assembled single molecule device via in sity growth of gold nanorods; (middle) nanoparticle dimers bridged by single molecules; (right) self-assembled nanoparticle heterodimer constituted of a truncated nanocube of palladium and a spherical gold nanoparticle [2, 3, 5].

featuring quantum interference effects at room temperature [7], as well as new approaches to control materials specific positioning of nanoparticles at surfaces [8].

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10:25 – 10:45

Towards Single Electron Nanoelectronics Using Self-Assembled DNA-Structure

K. Tapio[1,*], J. Leppiniemi[2], B. Shen[1], V. P. Hytönen[2], W. Fritzsche[3] and J. J. Toppari[1]

[1]*University of Jyvaskyla, Department of Physics, Nanoscience Center, P. O. Box 35, FI-40014 University of Jyväskylä, Finland*
[2]*BioMediTech, University of Tampere, Biokatu 6, FI-33520 Tampere, Finland and Fimlab laboratories, Biokatu 4, FI-33520 Tampere, Finland*
[3]*Leibniz Institute of Photonic Technology (IPHT), Albert-Einstein-Strasse 9, Jena 07745, Germany*
**E-mail: kosti.t.o.tapio@jyu.fi*

Single electron devices, especially single electron transistor (SET), could provide a huge leap forward in electronics and technology. However, in order to function properly up to room temperature, the physical dimensions of SET metallic islands need to be about ten nanometers or smaller, which is hardly possible by conventional top down fabrication methods, e.g., e-beam

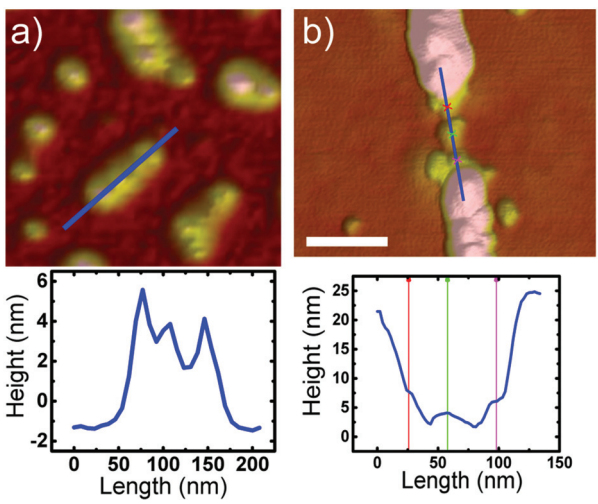

Figure 1 a) An AFM image of a TX-tile structure conjugated with three AuNPs on a mica surface. b) An AFM image of a dielectrophoretically trapped TX-tile-AuNP structure. The AuNPs, which are highlighted by the different colored crosses matching the vertical lines in the AFM cross section data, form a linear chain between the two fingertip eletrodes. The scale bar is 100 nm.

lithography. Meanwhile, bottom up methods have become more accessible for fabrication of metallic, nanoscale structures, where the DNA has proven to be a promising molecule due to its superior bottom-up self-assembly properties, and the fabrication of metallic nanostructures under 100 nm with the help of DNA is already well established [1]. In addition, DNA structures can be easily modified to incorporate different molecules and especially metallic nanoparticles with precise positioning.

There exist previously reported attempts to build SETs via DNA self-assembly even more than ten years ago, but without any electrical characterization [2, 3]. In this work we overcome the challenges of that time by using a highly defined TX-tile structure [4] and precise attachment of three gold nanoparticles via sticky ends (see Figure 1a). This conjugated structure was subsequently trapped using dielectrophoresis (see Figure 1b) for IV-characterization.

The trapped TX-tile-AuNP structure exhibited non-conducting behavior, which was most probably due to too large air gaps between the gold

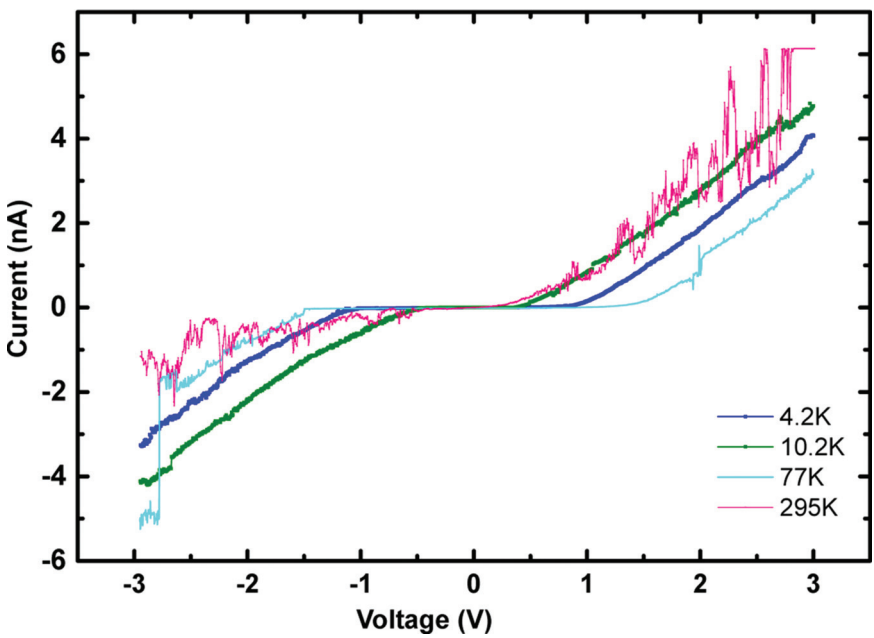

Figure 2 IV-characteristics of a sample similar as in the Figure 1b after several gold growth steps. The sample exhibits clear Coulomb blockade behavior with threshold voltages of –2 V and +1 V from 4.2 K up to room temperature.

nanoparticles. The gaps were then minimized by extra chemical gold growth step (nanoprobes gold enhancement kit). After the gold growth, the measurements revealed Coulomb blockade behavior (see Figure 2) which is the prerequisite for a functioning SET, from 4.2 Kelvin all the way up to room temperature.

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11:00 – 11:20

HOPG as a Substrate for High-Resolution AFM of Biopolymers

Dmitry Klinov*, Nikolay Barinov, Anna Protopopova and Evgeniy V. Dubrovin

Scientific Research Institute of Physical-Chemical Medicine, Laboratory of Medical Nanotechnologies, Moscow, Russia
**E-mail: klinov.dmitry@mail.ru*

The most common substrate for the AFM analysis of protein structure is mica. It is known that the surface of freshly cleaved mica is covered with a salt layer in the presence of water (including ambient conditions). It is therefore easy to expect that some part of biomolecules could be hidden within the salt layer on mica. We also note that in most publications, the height of biopolymers (DNA, for example, or fibrinogen) on mica is lower than their height on any other surface except polylysine despite the salt layer.

HOPG is another frequently used substrate in AFM, while few researchers pay attention to the high hydrophobicity of the surface. It is not obvious that a water-soluble protein should keep the proper initial conformation during absorption from the buffer solution onto the hydrophobic substrate. For example, fibrinogen adsorption onto the surface of freshly cleaved HOPG has been investigated: it is unsurprising that the height and morphology of the molecules indicated an essential denaturing of fibrinogen during absorption (Figure 1).

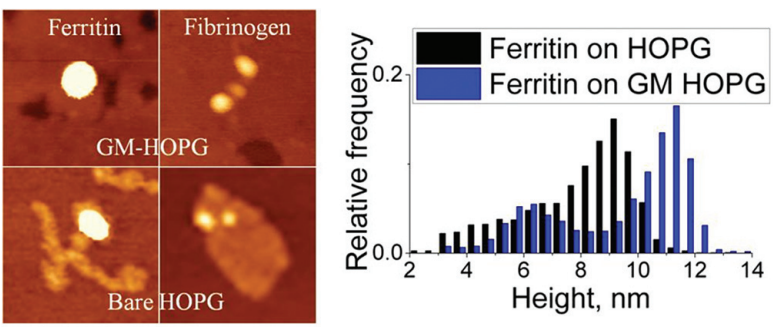

Figure 1 AFM images (left) and height distributions (right) of ferritin and fibrinogen molecules adsorbed onto bare HOPG and GM-HOPG.

In this study, high-resolution AFM was applied for direct visualization of the conformational transformations at the adsorption on HOPG surface at the level of single protein molecules. For this purpose, we have studied proteins of high biological and medical relevance, i.e. ferritin, fibrinogen, HSA and IgG. For comparison, the AFM measurements were also conducted for these proteins adsorbed on the HOPG surface covered by amphiphilic monolayer (GM-HOPG), which is moderately hydrophilic. In addition, the conformational behavior of ferritin and fibrinogen cross-linked by gluaraldehyde and adsorbed on HOPG was also studied. We have confirmed partial denaturation for all studied proteins upon their adsorption on HOPG, whereas they retained globular structure on GM-HOPG. The key approach was to use a modified HOPG surface as a substrate for fibrinogen adsorption. The surface of freshly cleaved HOPG has been rendered hydrophilic with the amphiphilic carbohydrate-glycine modifier called GM. The modified surface

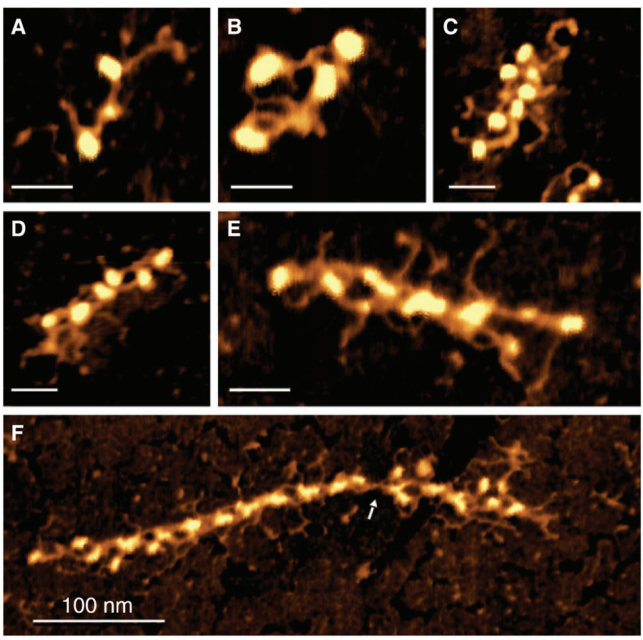

Figure 2 High-resolution AFM images illustrating the stepwise growth of protofibril. (A) One fibrin molecule with aC regions spread out. (B) Two molecules connected by both D-E interactions and aC regions. (C) Three molecules forming a D-E-D triad. (D) Four molecules. (E) Five molecules. (F) A long protofibril with 15 molecules and one structure mismatch marked by an arrow. The length of the scale bars in A-E is 30 nm.

provides favorable conditions for protein absorption and allows obtaining high-resolution images in an air environment. We used unique supersharp cantilevers [1–4] for a resolution as high as possible. Noteworthy, the heights of all studied proteins adsorbed on GM-HOPG are even slightly larger than those measured on mica, which is frequently used for protein deposition.

Thus GM-HOPG demonstrates the weaker distortion of protein conformation than mica. This observation is experimentally important for the precise estimation of the protein non-disturbed vertical dimensions by AFM technique. The observation of the HOPG induced denaturation of the proteins studied in the present report allows one to suppose that it is not specific to a protein structure and may take place for other "soft" globular proteins, which are characterized by the ability of the relatively easy structural relaxation.

Acknowledgment

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11:20 – 11:40

Controlling Deposition of Nanoparticles by Tuning Surface Charge of SiO_2 by Surface Modifications

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Self-assembly of nanoparticles on substrates is relevant for a variety of applications such as plasmonics, sensing devices and nanometer-sized electronics. We investigate the deposition of 60 nm spherical Au nanoparticles onto silicon dioxide (SiO_2) substrates by changing the chemical treatment of the substrate and by that altering the surface charge. The deposition is characterized by scanning electron microscopy (SEM). Kelvin probe force microscopy (KPFM) was used to characterize the surface workfunction. The underlying physics involved in the deposition of nanoparticles was described by a model based on Derjaguin-Landau-Verwey-Overbeek (DLVO) theory combined with random sequential adsorption (RSA). The spatial statistical method Ripley's K-function was used to verify the DLVO-RSA model (ERSA). This method can be used in future research to predict the deposition densities of charged nanoparticles onto charged surfaces.

Several techniques are available when it comes to the deposition of nanoparticles on substrates. It is for instance possible to deposit uniform nanoparticles in aerosol directly onto a substrate. These techniques require a special setup and it is important that the particles are deposited directly after production [1, 2]. Several reports have shown that it possible to deposit particles via convective assembly [3, 4], as well as directly from solution directly onto surfaces.

There is a large variety of parameters which are known to affect the density and nearest neighbor distance of deposited nanoparticles, both the characteristics of the nanoparticle dispersion such as concentration of particles, ionic strength, the valency of the ions as well as the size of the particles [5, 6].

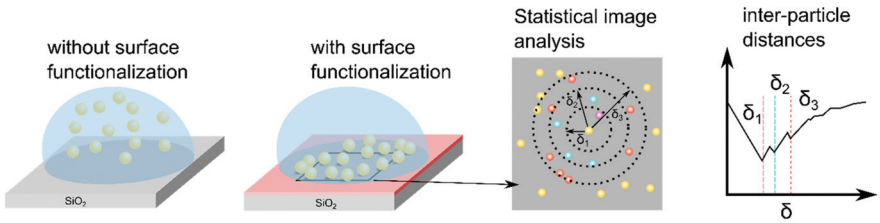

Figure 1 Top-left, particle deposition on clean Si/SiO_2. Top-right, particle deposition on Si/SiO_2 functionalized with APTES or PLL-HBr. Bottom-left and bottom-right, principal of statistical image analysis.

In addition stabilizing ligands, surface charge, presence of oxide and temperature can also alter the deposition [7, 8].

The particle-particle interactions and the substrate-particle interactions are believed to be important for the deposition of nanoparticles [6]. It is known that the densities of citrate stabilized nanoparticles on Si or SiO_2 are small after deposition [9], it is also known that a significant increase in particle density can be observed after different types of activation [10]. Citrate is a trivalent negatively charged ion, which adsorbs to the nanoparticle surface keeping them suspended in an aqueous dispersion.

In this work we explore the parameter space involved in the deposition of charge-stabilized nanoparticles. We investigate if there is a correlation between surface conditions and the density of particles and nearest neighbor distance after deposition. This was achieved by functionalizing substrates with different chemicals (APTES or PLL-HBr) as well as different doping of the underlying silicon. The nanoparticles were characterized using scanning electron microscope (SEM) and further analyzed using a statistical image processing software. The substrate surface potentials were investigated using kelvin force probe microscopy (KPFM) and a physical model to explain the mechanism behind the deposition of the nanoparticles based on Derjaguin-Landau-Verwey-Overbeek (DLVO) theory combined with random sequential adsorption (RSA) was developed. This is also known as the extended random sequential adsorption model (ERSA).

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11:40 – 12:00

Photo/Thermal Switching of a Norbornadiene: Towards Molecular Electronics Application

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Since its first inception to use rationally designed molecules for molecular electronics about 40 years ago [1], the field of single molecule electronics have made several strides. The key enabling component in this field are photoswitchable molecules. Photoswitchable molecules are molecules that can interconvert between two stable isomers usinglightas a stimuli. There are various types of molecular photoswitches that has been investigated for molecular electronics. The most notable ones are azobenzenes [2], diarylethenes [3], spiropyrans [4] and the DHA-VHF [5] systems.Despite some theoretical [6] and experimental [7] studies to use norbornadienes as a photoswitch, to the best of our knowledge, there is no report to use it as molecular photoswitch by anchoring it between two electrodes. Here, we report on the synthesisand characterization of norbornadiene-based molecular photoswitch (Figure 1).

The synthesis is started by first making 2,3-dibromonornorbornadiene from the commercially available norbornadiene using tosylbromide as a brominating agent [8]. Subsequently, the dibromimde was coupled toone side

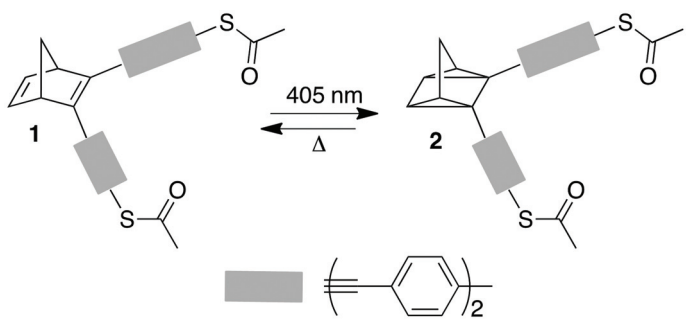

Figure 1 Photo(thermo)chromic reaction of norbornadiene photoswitch. Upon absorption of 405 nm light the norbornadiene form **1** isomerizes to the valence isomer quadricyclane form **2**. In the presence of heat **2** relaxes back to **1**.

triisopropylsilyl (TIPS) protected 1,4-ethynylbenzene through Sonogashira reaction. Finally, deprotection of the TIPS group followed by another Sonogashira reaction resulted in the attachment of the anchoring thioacetate groups. The product was confirmed by NMR, IR spectra as well as elemental analysis. From its proton NMR the olefinic protons as well as the protons on the bridge head are observed around their characteristic positions. The protons for the methyl groups of the thioacetate anchoring groups are observed at 2.44 ppm. From the ^{13}C NMR, the *sp* hybrid carbons were identified between 88 and 103 ppm.

To study its absorption spectra and its photoswitchability, **1** was dissolved in toluene. From the absorption spectra two maxima could be observed at 332 nm and 395 nm with a shoulder. Upon irradiation at 405 nm, the second maxima starts disappearing resulting in only one maxima left around 320 nm. Apparently, this is light initiated 2+2 cycloaddition reaction converting the norbornadiene form **1** to the quadricyclane form **2** [9].

In this work we synthesized and investigated rationally designed norbornadiene-based photoswitch molecule **1**. NMR, IR and elemental analysis confirmed the product. UV-vis study of the molecule shows **1** has a potential for use as a photoswitch molecule in single molecule electronics.

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12:40 – 13:20

Plasmonic Nanostructures Based on DNA Origami Silhouettes

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The interest in plasmonic nanostructures has grown rapidly due to their unique optical properties and achievable field enhancement. However, due to limitations of the conventional nanofabrication methods nanostructures with tunable plasmonic activity in visible range are hard to fabricate. Yet, DNA self-assembly, especially DNA origami [1], provides a precise and programmable way to form nanoscale structures. However, utilization of DNA constructions to fabricate plasmonic nanostructure [2] is still very challenging since the DNA molecules themselves are not conducting and despite many attempts not easy to metallize with high enough accuracy [3].

Here we demonstrate a novel method, which takes advantage of the DNA origami constructions and together with conventional nanofabrication processes enables fabrication of high quality sub-100-nanometer plasmonic nanostructures with desired shapes [4]. The method employs DNA origami silhouettes formed in a silicon dioxide layer by DNA selective chemical vapor deposition process [5]. Metal is subsequently evaporated onto the substrate through the formed silicon dioxide mask to form nanostructures with the same shape as the DNA origami. The resulting metallic nanostructures have a feature size smaller than 20 nm which is already comparable to the e-beam lithography. In order to take full advantage of this highly parallel method and to expand the fabrication to an even larger scale in a cost-effective way, we have demonstrated that DNA origami can be deposited onto large areas on any material with a spray-coating method [6].

Furthermore, we have successfully fabricated functional optical antennas with a tunable plasmonic resonance in visible range by this method, as shown

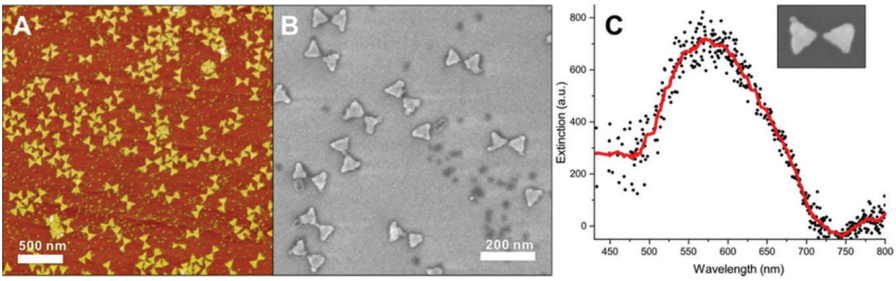

Figure 1 (A) AFM micrograph of "bowtie" DNA origamis on mica (B) SEM micrograph of the Au bowtie antennas on sapphire (C) Localized surface plasmon spectrum of an individual bowtie antenna (see inset).

in Figure 1. A pair of Au triangles pointing against each other with a sub-10-nm to 20 nm gap in between can be patterned with a single bowtie-shaped DNA origami. The fabricated bowtie structures have sharp plasmonic resonance, tunable via gap length, and high SERS activity [7]. This ability to fabricate dimers or even multimers of metallic nanoparticles with designed shape and arrangement provides great potential in various applications, especially sensing and metamaterial fabrication.

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13:20 – 14:00

Conformations and Dynamics of DNA based Devices

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DNA has been used as a building block in the design and assembly of a number of DNA devices, whose operation is often based on conformational changes between several states [1]. Sizes range from a few nanometers to several hundreds of nanometers. Förster resonance energy transfer (FRET) spectroscopy is a powerful tool to investigate structural dynamics properties of these DNA-based devices. Furthermore, individual molecules can be followed in action by single molecule microscopy and thus allow a direct view of how they work. I will discuss in this talk our implementation of these methods [2] for investigating DNA based devices, such as a DNA actuator device consisting of two piston arms that can move with respect to each other with sub-nanometre steps and a total movement of 7 nm [3] and a DNA origami box, a nanocontainer whose lid can be opened and closed with DNA triggers [4] (Figure 1). Our results give a direct insight into the movement, conformation changes and performance of these DNA devices.

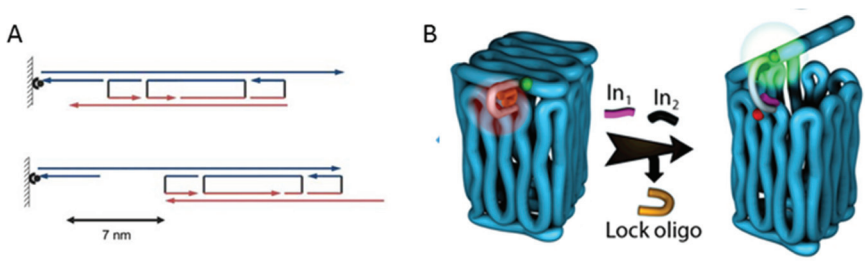

Figure 1 Schematic representation of A) the surface immobilized DNA actuator in two different conformations giving a total movement of 7 nm [2]. The two piston arms are shown in blue and red respectively. B) the DNA origami box with one lock shown in closed and opened conformation. Fluorophores, attached for FRET studies, are shown as green and red dots [3].

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14:00 – 14:20

Conjugation of Gold Nanoparticles onto a 42 Helix-Bundle DNA Origami Structure

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In this study, the precise placement of gold nanoparticles onto a self-assembled DNA nanostructure was investigated. The structure was designed using the scaffold-based DNA origami method popularized by Paul Rothemund where oligonucleotides (staple strands) connect regions of long single-stranded DNA by staple-strand cross-overs thereby forming predefined geometrical shapes [1]. Origami formation was achieved by treating folding solutions to either standard thermal annealing ramps or isothermal protocols.

Nanoparticle conjugation was accomplished by gold nanoparticle/poly-dT ssDNA conjugates coupled to selected staple-strands modified with poly-dA overhang sequences. From AFM imaging, the conjugation success was found to surpass a 90% yield with individual origami structures containing either one or two nanoparticles with precise geometrical placement. As the placement

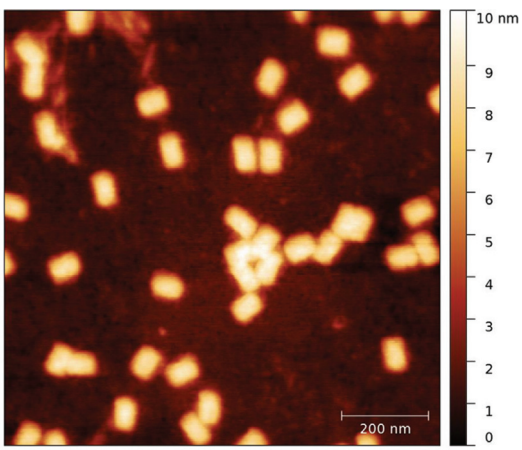

Figure 1 AFM image of the 42 hb structure.

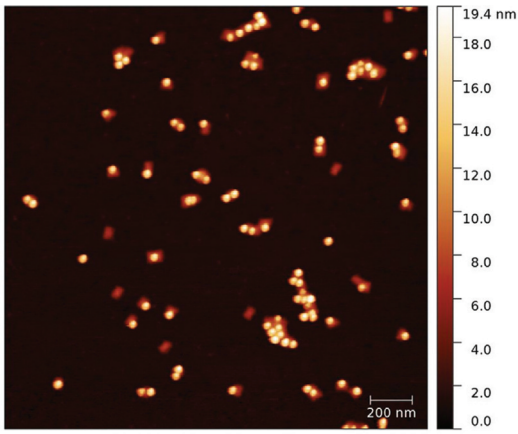

Figure 2 AFM image of the origami/nanoparticle conjugates.

of staple-strand overhangs is highly customizable, this approach allows the possibility of arranging nanoparticles into different patterns in few steps.

A potential application includes the optical studies of nanoparticle-fluorophore interactions resulting in fluorescence enhancement/quenching possibly useful for sensor applications.

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14:35 – 15:15

Delivery Vehicles Based on DNA Origami

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Recent progress in structural DNA nanotechnology has opened up numerous opportunities to use well-defined DNA nanostructures in a variety of bioapplications [1, 2]. Using customized DNA structures as smart biochemical nanodevices [3] and targeting cells with DNA-based drug delivery vehicles [4] are arguably some of the most intriguing implementations.

Along these lines, we have recently studied how active enzymes could be delivered into HEK293 cells *in vitro* when they are attached to a tubular DNA origami (Figure 1) [5, 6]. We employed bioluminescent Lucia luciferase enzymes as a cargo and monitored the activity of these delivered enzymes

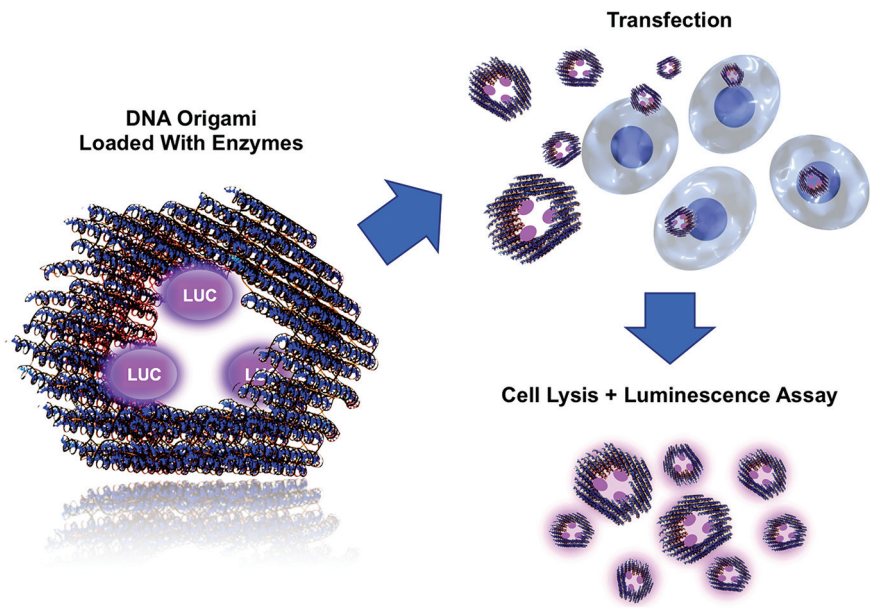

Figure 1 A tubular DNA origami can be loaded by bioluminescent enzymes and transported into cells. The activity of delivered enzymes can be monitored using luminescence assay [6].

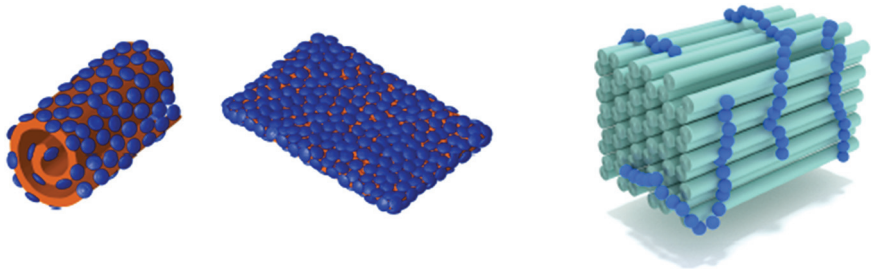

Figure 2 Left: Rectangular DNA origamis are encapsulated using CCMV capsid proteins [7]. Right: A brick-like DNA origami is coated with cationic block-copolymers [8].

from a cell lysate using a coelenterazine-based luminescence assay [6]. The results show that the enzymes stay intact and retain activity in the transfection process. Owing to the modularity of DNA origami, the proposed technique could become applicable for advanced drug-delivery and therapeutics, such as enzyme replacement therapy.

Furthermore, to expectedly increase the transfection rates and to improve the stability of DNA nanostructures in biological environment, we have tested different DNA origami coating techniques. Previously, we have demonstrated how 2D DNA origamis can be encapsulated with virus capsid proteins in order to enhance cell transfection rates (Figure 2, left) [7]. Very recently, we have created polymer-DNA origami-complexes by combining 3D DNA origamis and cationic block-copolymers (Figure 2, right) [8]. In this work, we studied the binding efficiency of polymers and used the formed polymer coatings to tune the enzymatic reaction rates of the abovementioned luciferase-loaded tubular DNA origamis. We observed that by adjusting the amount of polymer used for the coating, it is possible to control the characteristic time constant of the luminescence decay.

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15:15 – 15:55

Luminescence from Molecular Ions *In Vacuo*

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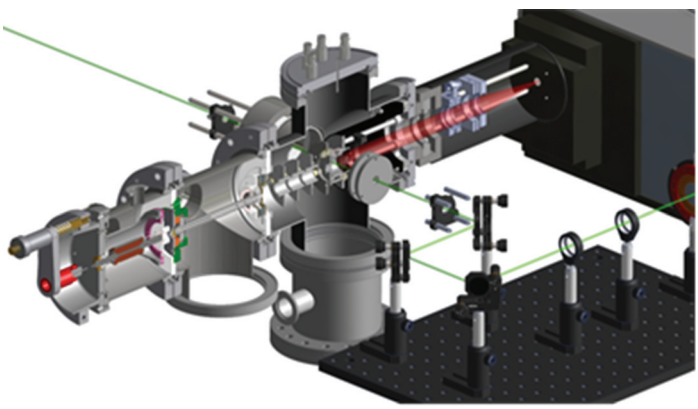
Gas-phase ion spectroscopy reveals the true colors of molecular ions and uncovers the perturbations by a microenvironment. Absorption spectra are recorded indirectly from ion dissociation or electron detachment (*i.e.*, action spectroscopy) as there are too few chromophore ions for traditional light transmission experiments. I will present some recent results on chlorophylls [1], the green pigments found in plants, and discuss the importance of binding a ligand axially to the magnesium center as well as the shift in absorption when two pigments talk to each other. Unfortunately, our results also show that it is difficult to photodissociate the rather big systems on the instrumental time scale (up to 10 μs). Another technique that does not rely on ion dissociation is luminescence spectroscopy where the photons emitted from the photoexcited ions are detected. We have recently constructed an instrument, called LUNA (Luminescence iNstrument in Aarhus) where ions are photoexcited in the center of a Paul trap followed by photon detection [2]. The setup benefits from a high photon collection efficiency, which is accomplished by using a cylindrical ion trap where one end-cap electrode is a mesh grid combined with an aspheric condenser lens. The geometry permits nearly 10% of the emitted light to be collected and, after transmission losses approximately 5% to be



delivered to the entrance of a grating spectrometer equipped with a detector array. The ions are produced by electrospray ionization allowing the study of fragile and/or large molecular ions. I will describe the instrument and present some recent findings.

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15:55 – 16:15

AFM Probing the Surface Chemistry Modifications under Ambient Conditions at Nanoscale

Jens P. Froning[1,2], Petr Lazar[1], Martin Pykal[1], Qiang Li[2], Mingdong Dong[2,*], Radek Zbořil[1], Michal Otyepka[1]

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Fast force spectroscopy allows not only topographical investigation of surfaces, further it is sensitive to surface chemical modifications even under standard ambient conditions in the laboratory. It is not surprising, when one considers atomic force microscopy an extended, electronic version of the sense of touch. But the 2D mapping detail of surface is. In a study we investigated the stepwise oxidation of graphene by Raman Spectroscopy, XPS and AFM, where AFM had the potential of probing and mapping

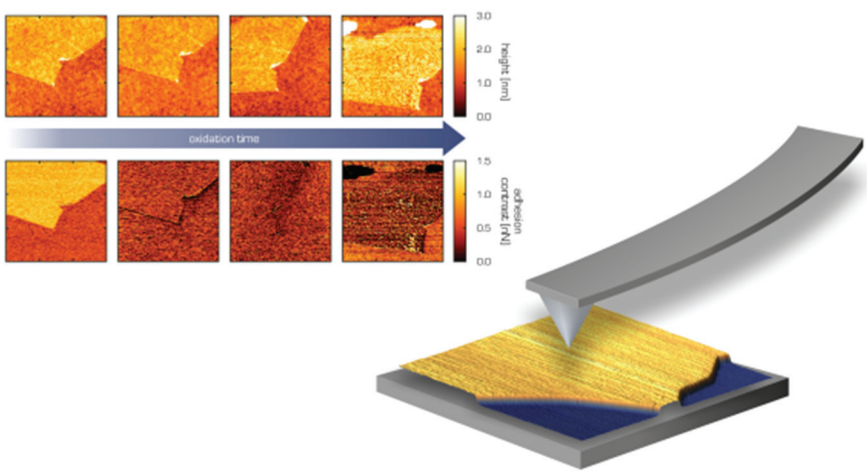

Figure 1 Graphical illustration of atomic force microscopy observations concerning the induced chemical modification of a surface. Here, a single layer graphene flake on silicon dioxide was treated with ozone and ultra violet light.

the local surface conditions in nanoscale dimensions. The results showed a gradual oxidation starting from the edges and defects of the graphene. XPS confirmed the overall change in oxidation. Theoretical simulations of the probe–surface system were needed to explain the measured behavior in the force mapping. Advanced force spectroscopy can give insight into a changing chemical surface in a more simple way, when paired with other characterization techniques.

16:30 – 17:10

MMX Molecular Wires

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We report on the electrical transport properties of platinum based MMX wires [1–3]. These molecular wires exhibit high electrical conductance over hundreds of nanometers (Figure 1). During the presentation I will briefly

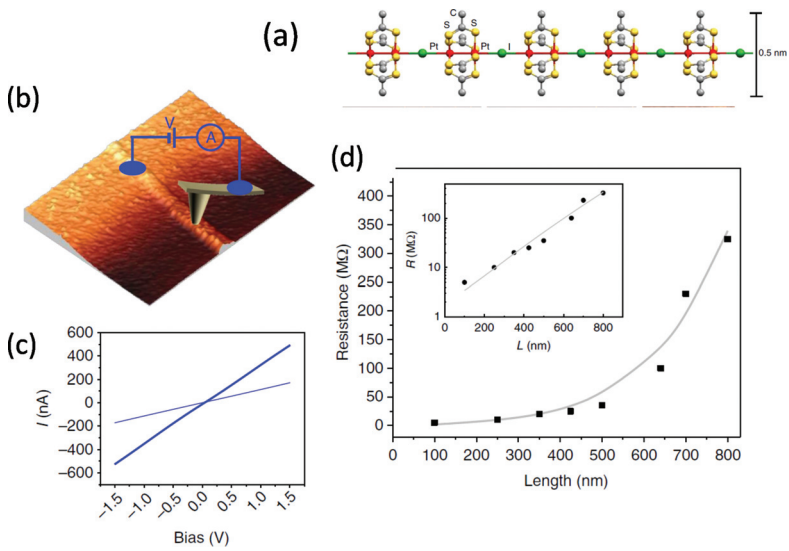

Figure 1 (a) Structure of a $[Pt_2(dta)_4I]_n$ (*dta* = dithioacetato) single fibre. (b) Scheme of the electronic circuit used to measure the current flowing through the nanoribbons, a metallized AFM tip is used as a mobile electrode. I/V curves obtained at different distances between electrodes (lengths) for the same nanoribbon. Here it can be clearly seen that the linear behaviour is maintained for every point. Resistance is calculated as the inverse of the slope of these graphs. (c) Resistance versus length, in a linear scale, for the same nanoribbons as data depicted in b. The inset displays a semilog plot of the same experimental data.

review the synthesis and on surface formation of the molecular structure and I will discuss the mechanism that influence their electrical transport properties.

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17:10 – 17:30

Single Molecule Studies of Amyloid β Oligomer Self-Assembly

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The self-assembly of Amyloid β (Aβ) proteins into aggregates, specifically soluble oligomers, in the brain is hallmark of the early onset of Alzheimer's disease (AD). While intensive efforts have been made to understand this process, the mechanism of how disordered monomers assemble into aggregates remains elusive. Several studies have shown the existence of β hairpin and turn structures in amyloid monomers, oligomers, and fibrils; however how these structures affect the assembly into aggregates remains elusive. To characterize the effect of β hairpins we have conducted single molecule studies of amyloid peptide consisting of an Aβ(14-23) monomer interacting with an Aβ(14-23) hairpin, and two Aβ(14-23) hairpins interacting. The hairpin was constructed using two Aβ(14-23) peptides linked with a β turn forming YNGK tetra peptide.

AFM based single molecule force spectroscopy experiments (SMFS) enabled direct measurements of the stabilities of these complexes and revealed higher stability for hairpin-monomer complex compared to the hairpin-hairpin complex, indicated by much larger unbinding forces for hairpin-monomer complex. To elucidate the molecular differences between the two complexes as well as fully characterize the interaction and assembly of the complexes we conducted long time-scale MD simulations. We were able to observe the self-assembly process for both complexes. Structures representing conformations observed in experiments were then selected using a novel validation approach based on comparison of simulated pulling data with data from AFM SMFS experiments [1]. Through this process, we identified a novel type of conformer for the monomer-hairpin complex. In this new conformation, the monomer is intercalated with the hairpin and forms a very stable complex. Overall, our study provides a fundamental step toward elucidating the Aβ structures, the assembly process, and understanding the role of pre-existing structure during the self-assembly process. Importantly, the developed validation approaches

for MD simulations are not limited to amyloid proteins, but can also be applied to other molecular systems.

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17:30 – 17:50

Self-Assembly Potential of the Designer Peptide RFFFR

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Self-assembly of protein nanostructures has attracted much interest due to its role in over 20 degenerative diseases such as Alzheimers, Parkinsons and prion diseases. Often the self-assembly is not particularly well understood and is investigated with isolated smaller peptides originating from the proteins involved, as a model system. One such motif is the LVFFA peptide derived from the ß-amyloid peptide involved in Alzheimers disease. Later, this motif was further shortened to the analog diphenylalanine (FF), which is capable of forming nanotubes, nanowires, films, vertical aligned wires and sponge-like structures [1]. In parallel, the triphenylalanine (FFF) peptide was studied, which forms plate-like structures with lengths of several micrometers or nanospheres without any void spaces [2].

However, few of these short peptides forms ordered structures resembling amyloid fibers. As to develop a model amyloid system a short virtual screening was performed. One of the peptides formed ordered fibers and was selected for further investigation [3]. The self-assembly was studied by coarse-grained and atomistic MD simulations with the MARTINI [4] and OPLS-aa [5] force fields, respectively. Semi-quantum mechanical calculations further verifies the obtained results and proves that the self-assembly was not a result of the force field parameters.

When the peptide was studied empirically, the peptide was observed to form fibers that entangled into spheres (Figure 1) [6]. The fiber morphology was consistent with what observed by simulations and several other experimental results could be explained by the computational results. As Kelvin probe force microscope show that the spheres have a surface potential comparable to that of a gold film, the spheres and fibers are likely electrically conductive and may be used as self-assembling biowires with a size comparable to DNA. Furthermore, since the spheres untangle into free fibers that dissolve over time, the spheres may be used as a drug-delivery system of hydrophobic drugs and controlled drug-release of drugs with a short lifetime.

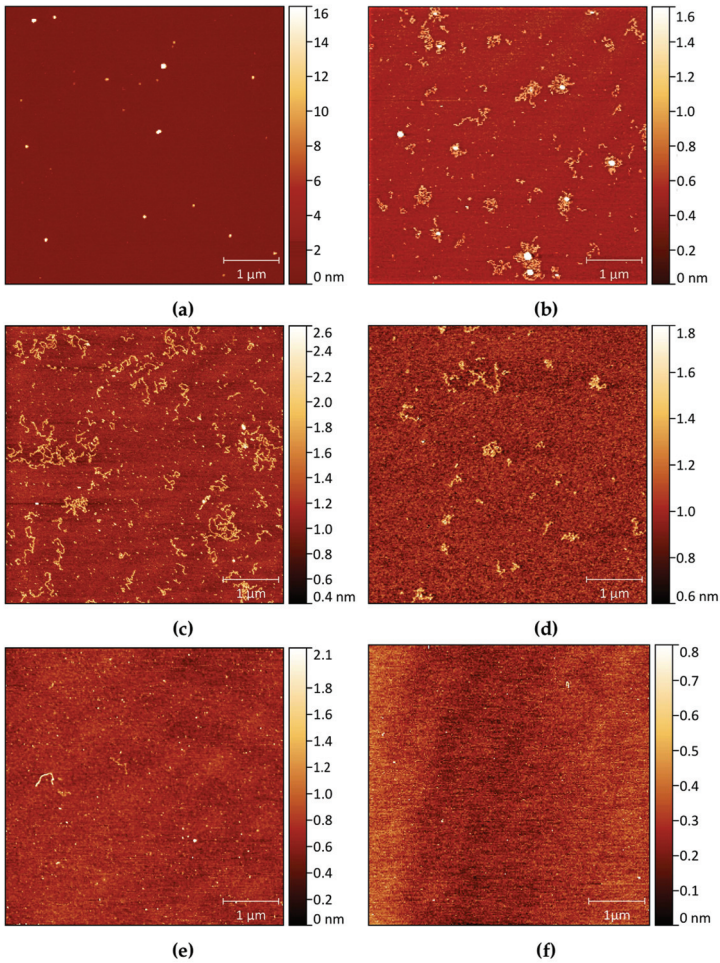

Figure 1 AFM measurements of 10 mM RFFFR solution diluted ti 1 mM and measured at different time intervals. (a) 0 min. (b) 30 min. (c) 60 min. (d) 120 min. (e) 240 min. (f) 480 min.

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17:50 – 18:30

Single Molecule Investigations on DNA Origami Platform

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DNA nanotechnology provides a robust method for building nanoscale architectures. The programmable surfaces of 2D DNA origami provide an idea functional template to control the spatial orientation of individual molecules in accurate position. Such programmable DNA surfaces can be utilized for investigating biological molecules at single molecule level. DNA–based platform strategies was successfully applied to single molecule manipulation, activities of enzymes, surface polymerization and molecular recognition. This approach will benefit not only for DNA nanotechnology, but also for single molecule detection.

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17/11/2016

09:00 – 09:40

Hampering D76N β2m Fibrillogenesis through Nanoparticles Interaction

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The interaction between proteins and nanoparticles (NPs) is becoming more and more central to several nanotechnological applications [1]. We have recently addressed the behavior of gold nanoparticles stabilized by a shell of citrate surfactants (Cit-AuNPs) with the amyloidogenic protein β_2-microglobulin (β2m) [2]. β2m is responsible for dialysis related amyloidosis (DRA) affecting long-term hemodialysed individuals [3]. Contrary to expectations, no clear aggregation promotion was detected in the presence of Cit-AuNPs, by NMR evidence showing that β2m globular structure is stable and that there is a protein domains preferentially involved in the interaction with the NP surface [2]. In this paper we report the influence of

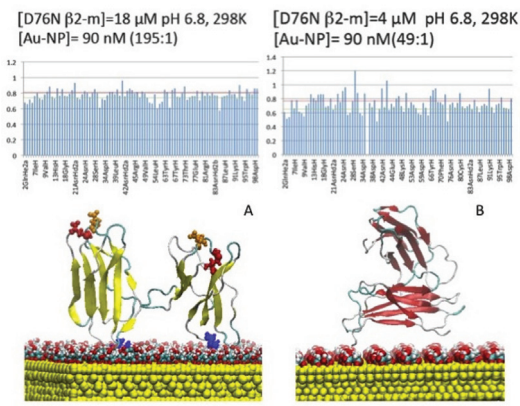

Figure 1 Dimers (A and B) of D76N protein interacting with citrate-capped gold nanoparticle: (top) NMR protein signal intensities; (bottom) Dimers on gold after 20 ns of T-REMD simulations.

NPs on the fibrillation process of β2m, using a naturally occurring mutant, namely D76N β2m with asparagine substitution for aspartate at position 76. This mutant has been shown to readily form amyloid fibrils *in vitro* under physiological extracellular conditions and to be responsible for an aggressive systemic amyloidosis. Its interaction with Cit-AuNPs was characterized by a comprehensive investigation including *multi-scale* modeling (classical atomistic molecular dynamics and rigid-body protein-surface docking), NMR and the fibril formation was analyzed by three different methods: thioflavin T fluorescence, native agarose gel electrophoresis and transmission electron miscroscopy. Our results indicate that AuNPs are able to inhibit D76N β2m fibrillogenesis through the formation of long-life complexes that competes with the binding to other proteins [4].

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09:40 – 10:20

Molecular Dynamic Simulations of Self-Assembling Peptides (SAPs)

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SAPs are very competitive biomaterials because they are easy and affordable to synthesize in addition to being naturally bioabsorbable. Their self-assembly mechanism relies on weak interactions (e.g. h-bonds and electrostatics) whose activation and arrangement depends on environmental conditions (e.g. pH and concentration) and may give rise to hierarchical nano-structuring (e.g. ribbons and tapes). [1] Different types of nano-structures yield to different morphology, self-healing ability and mechanical properties that, in principle, may be tuned to obtain synthetic and biomimetic extra cellular matrices compatible with the target tissue, the nervous one after a spinal cord injury

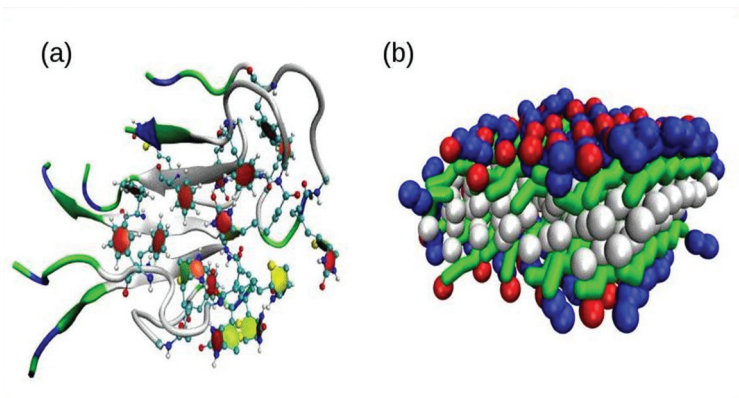

Figure 1 SAPs sampled by (a) united atom and (b) coarse-grained molecular dynamics simulations.

in our case. [2] Indeed mastering amino acid sequence and environmental conditions to obtain a precise final product is not trivial. Computer simulations are increasingly recognized as a valid and powerful support to experimental investigations in the field of supramolecular materials. To gain a deep understanding at molecular level about the role played by sequence and environmental conditions on two families of peptides developed in our labs [3, 4] we performed molecular dynamics simulations from united atom to coarse grained levels with increasing times and system sizes. The role played by different residues is mainly described in terms of aggregation ability, β-structuring propensity and alignment ability. The simulations on different levels allowed us to recognize the importance of biotinylation [3] and the driving role of electrostatic interactions [4] as the main elements in the different self-assembling behavior of the tested peptides. The two types of simulations clearly highlighted advantages and limits treated at different level of accuracy.

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10:35 – 11:15

Electronic Circular Dichroism on the Inter-Base Pair Scale: From Oligonucleotides to Nucleosomal DNA

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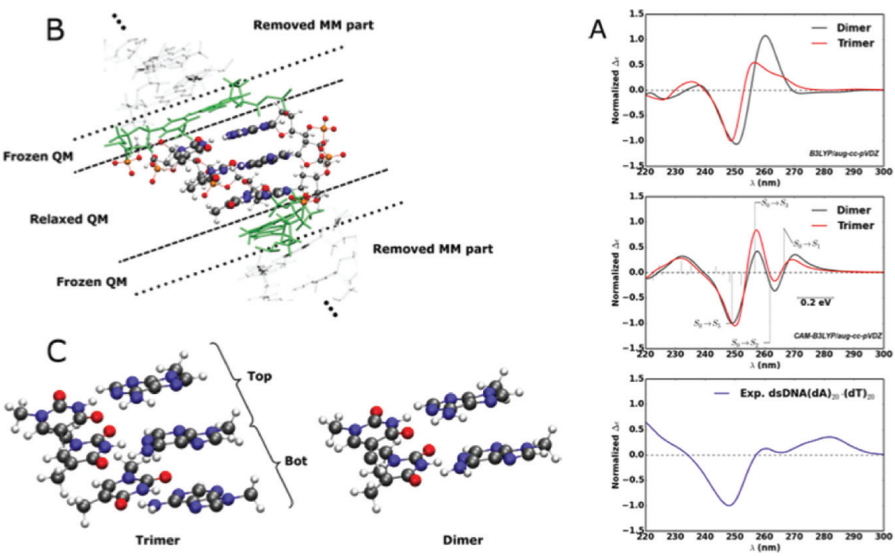
The perfect double-helical conformation of DNA and its biochemical properties can be altered by its surrounding environment (*e.g.*, ion concentration, interactions with solvent or supramolecular complexes with proteins such as histones). The prediction of its conformation is thus crucial to understand DNA biochemical processes.

Over the past years, circular dichroism has been widely used to elucidate the helical structure of DNA in solution [1]. Theoretical CD calculations are relevant to rationalize and forecast DNA chirality at the nanoscale. However, computational time appears as a bottleneck for calculating the



entire DNA CD-spectra regarding to the size of the system. The present work aims at providing an efficient methodology by (i) considering a minimal model system and (ii) assessing available computational methods.

On one hand, DNA was sequentially reduced to either base pair dimer or trimer. CD calculations exhibited that the former cutting (i.e., two-body approach) is sufficient with respect to previous study [2] and experiments. On the other hand, the high density of states prevents the calculation of entire CD spectra by classical TD-DFT. The complex polarization propagator (CPP) is a relevant alternative for such calculations [3]. Several functionals and basis set were assessed on the base pair model. Finally, the aforesaid two-body approach with the appropriate CPP-DFT method was applied on DNA structures from (i) MD simulations [4] and (ii) a nucleosomal crystallographic structure [5].

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11:15 – 11:55

Nanotextured Surfaces with Enhanced Optical and Thermodynamic Properties Fabricated by a Maskless Reactive Ion Etching Method

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We discuss a simple method for one-step maskless fabrication of nanotextured surfaces in Si and replication of such surfaces in polymer. The nanotextures are fabricated on silicon wafers by using a simple one-step method of reactive ion etching at different processing time and gas flow rates. Reactive ion etching (RIE) is a dry etching technique that can be used to structure silicon surfaces without masks through the combined effect of a corrosive gas (SF_6 and/or CH_4) and a passivating gas (O_2) [1]. Depending on specific process

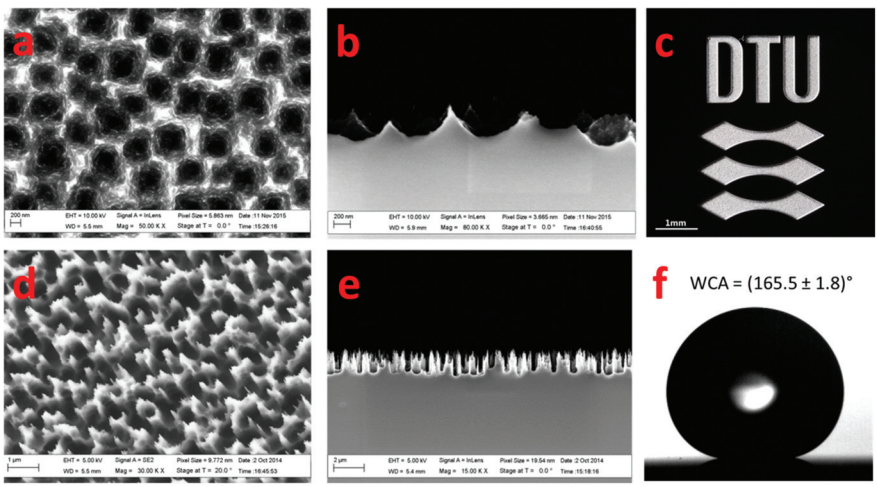

Figure 1 a) Top view Scanning electron micrograph (SEM) of inverted pyramid "white Si" structure. b) Same structure as a) in cross-section view SEM. c) DTU logo fabricated with "white" and "black" Si nanotexture. d) 20º tilted view SEM of nanograss texture. f) Same structure as d) in cross-section view SEM. Micro-droplet resting on FDTS coated nanograss textured Si surface.

parameters, the nanotexture can be tuned to have different optical surface properties ranging from spiky nanograss yielding antireflective mat-black surfaces (black Si) to inverted nanopyramids yielding distinct milky white surfaces [2]. Moreover, by subsequently coating the surfaces with hydrophobic 1H,1H,2H,2H-perflourodecyltrichlorosilane (FDTS) [3] or applying an oxygen plasma treatment, the wetting properties of the surfaces can become superhydrophobic or superhydrophillic respectively. Strong anti-wetting behaviour can also be obtained by replicating the nanograss in hydrophobic polymer such as polypropylene (PP). To showcase the feasibility of the polymer replication, we demonstrated large area roll-to-roll (R2R) replication of nanograss by employing an industrial extrusion coating process [4] to fabricate superhydrophobic PP polymer foils with water contact angles approaching 160° and droplet roll-off angles below 10° [5].

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12:40 – 13:20

Self–Assembled Diphenylalanine Peptide Nanostructures for Optimized Cell Culturing and Sensing

Winnie E. Svendsen[1,*], Tanya Bakmand[1], Anne Byriel Walls[2], Helle S. Waagepetersen[2], Jaime Castillo-Leon[3] and Maria Dimaki[1]

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In this paper we report the use of Self-Assembled Diphenylalanine Peptide Nanostructures in cellular culturing platforms in a microfluidic setting for optimized control, more *in vivo* like culturing conditions, biocompatibility and enhanced monitoring possibilities. We have developed a set-up using vertically aligned diphenylalanine peptide coatings to optimize cellular growth, initially tested on Hela cell lines [1] and further developed to culture the mouse neuronal cell line PC12 [2]. Finally, we tested how culturing of primary neocortical neurons on diphenylalanine peptides affected cell viability and cellular glucose metabolism. We have observed enhanced growth and amplified signal intensity in electrochemical sensing scenarios [2].

The standard methods applied today to culture cells do not represent the *in vivo* situation in any way. Cells are cultured on a flat surface in a static

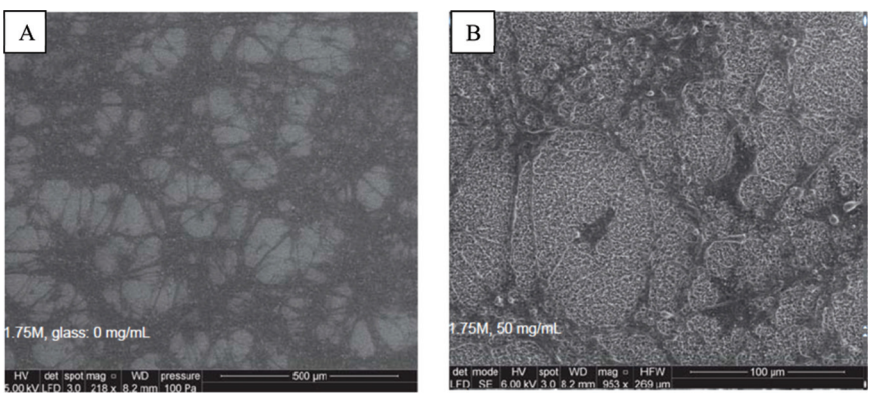

Figure 1 (A) Cells grown on glass seem to migrate into islands. (B) Cells grown on the peptides show increased homogeneity and are well connected.

liquid and the necessary nutrients for the growth are provided every 2 to 3 days with a complete change of medium. That means that cells are growing in a nutrient rich medium with no waste removal. In reality, cells in mammals grow in a complex 3D environment with a continuous exchange of nutrients and removal of waste.

Silicon, gallium phosphate, platinum and other nonorganic nanostructures have been used to explore cell attachment and spreading behavior. However, fabrication of such nanostructures requires specialized equipment or clean-room conditions, which increases the fabrication cost and time; there are also several possible toxicity issues raised for these substrate materials and therefore their use yields some limitation, as discussed in [2]. Self-assembled peptides are biological building blocks able to self-organize into a variety of nanostructures. Diphenylalanine is a short dipeptide that can be used for the synthesis of self-assembled structures, such as nanotubes or nanofibers under very mild conditions. These structures have been structurally, electrically and chemically characterized. The use of these biological nanostructures for applications, such as the development of biosensors, the fabrication of new nanostructures, as well as cell culturing has been described. Our group recently reported on the growth of HeLa and PC12 cells in vertically aligned self-assembled peptide nanofibers, as well as the design of a combined cell culture-biosensing platform where self-assembled nanofibers were patterned next to a traditionally used functionalized gold transducer for the detection of dopamine from PC12 cells. The structures created by these peptides provide a more 3D environment which is biocompatible, and these 3D surfaces provide a better cell adhesion and survival compared to the flat surfaces. Apart from

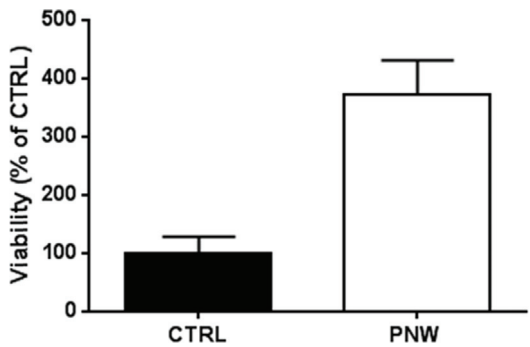

Figure 2 Viability graph showing neocortical neurons cultured for 7 days, using LDH activity as viability indicator.

our results with HeLa and PC12 cell lines, we have also cultured primary neuron cells on these surfaces. The results suggest an enhanced growth on the peptide nanostructures compared to the standard methods. Further viability studies for neuron cultures for seven days, using lactate dehydrogenase (LHD) activity as an indicator, showed neuron cultured on peptides nanowire exhibit a significantly better survival rate compared to the 2D cultures (Figure 2).

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13:20 – 14:00

Exploring Electrical Functionality in Metal Ion-Intercalated Non-Canonical DNA Duplexes

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The remarkable properties of DNA, in both its natural role as the embodiment of the genetic code for all living organisms and its potential "off-label" use in technological applications, can be attributed, in large part, to its unique base-pairing rules. These rules have enabled such breakthroughs as structural DNA nanotechnology, DNA computing and DNA-based molecular electronics. In this work, we are exploring the potential afforded by violating canonical base-pairing rules.

In 2002 Tanaka et al. reported that cytosine-cytosine (C-C) mismatches could be "paired" by inserting a Ag^+ ion at the site of the mismatch [1]. The sequence gap left between two mismatched pyrimidines allows for a coordination bond between the opposing amine groups and a metal ion (Figure 1A). Miyake et al. extended this approach to $Hg2^+$ ions inserted at thymine-thymine sites [2] whilst maintaining the conformation of the conventional Watson-Crick duplex [3]. These results suggest that it may be possible to create a string of concatenated metallic ions within a DNA duplex framework. We have recently synthesized molecular wires in this fashion and have been studying their emergent chemical, structural and electrical properties.

Thermal melting confirms that highly mismatched duplexes can indeed be formed in the presence of Ag^+ ions, with lengths up to $\sim$10 nm (30 consecutive C-C mismatches), as shown in Figure 1B. These can be ligated to form even longer (up to 75 nm) wires. STM break junction measurements of wires with 11 C-C mismatches show clear evidence of increased conductance relative to their canonical counterparts [4]. Other single-molecule conductance platforms are presently being pursued to further characterize the electrical properties of these wires.

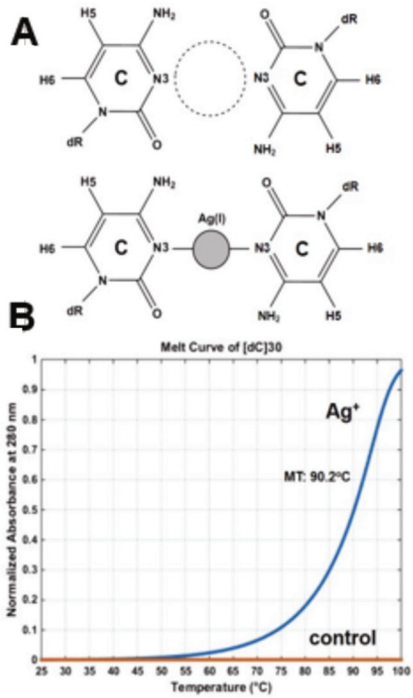

Figure 1 (A) Structure of C-C mismatch predicted from NMR studies. Top: unbound with gap. Bottom: bound to Ag^+ at N3 position to form the dC:Ag^+:dC metal pair. (B) Melt curves showing absorbance at 280 nm over increasing temperature both with and without a saturating level of Ag^+ for the 30-base poly-cytosine. This duplex melts at >90°C.

In addition to the prospect of enhanced electrical properties, metal-containing DNA oligomers present intriguing possibilities for the creation of self-assembled nanostructures. The usual tools for designing such structures are limited for these molecules, as they do not allow for the inclusion of mismatched bases and their associated thermodynamic stress on the system. We have therefore developed a new set of algorithms that enable the design of complex sequences with non-canonical base-pairing rules for the self-assembly of geometrically-complex, functional duplexes. We hope to use these for the programmed generation of heterogeneous, electrically-active DNA nanostructures.

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14:00 – 14:20

Fabricating Nanoscale Circuits with On-Origami Nanolithography

Sisi Jia[1,†], Jianbang Wang[2,†], Huajie Liu[2,*], Jie Chao[3], Shao Su[3], Lianhui Wang[2], Wei Huang[3], Kurt Gothelf[4] and Chunhai Fan[2,*]

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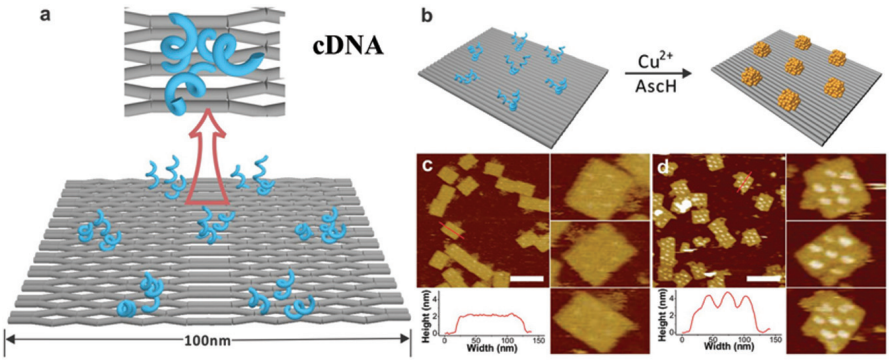
DNA nanotechnology offers great potential for bottom-up fabricating nanoscale optical and electronic devices in a "soft lithographic" approach [1, 2]. Nevertheless, all previous methods rely on metal plating of nanoparticle seeds pre-loaded on sites of self-assembled DNA nanostructures, which often leads to defects and hetegeniety [3, 4]. Here we devised a metal-seed-free on-origami nanolithographic (MSFOON) strategy to directly metallize DNA origami nanostructures on prescribed positions with high site-specificity and nanometer resolution. We found that DNA in different forms exhibited distinct condensation abilities in the presence of metal ion atmosphere. By exploiting this intrinsic DNA-metal ion interaction, we could selectively metallize single-stranded protruding clustered DNA (pcDNA) on double-stranded DNA-based two-dimensional origami substrates. With the introduction of pcDNA on prescribed positions of the origami "canvas", we could fabricate a variety of copper and silver nanopatterns ranging from 0-D dot, 1-D wire to 2-D shape using MSFOON. More specifically, we fabricated a series of nanopatterns with line width of 10 nm on the origami, analogous to "lumped" nanocircuits [5]. We expect that this MSFOON strategy sheds new light on DNA origami-based fabrication of nanoscale circuits for electronic and photonic applications [6].



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14:35 – 15:15

Enzymatic Synthesis of Designer DNA: New Templates for Directed Assembly

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The enzymatic synthesis of long DNA with a controllable sequence, length and functional content will be presented. A modified PCR protocol using the key components of a repeating sequence oligo-seed (ca.20 bases), the deoxynucleotide triphosphates (dNTPs), and a DNA polymerase is reported. Using a thermostable *Thermococcus gorgonarius* Family B DNA polymerase exonuclease minus variant, Z3, and 20 heat-cool cycles, long DNA up to 20,000 base pairs bearing repeating units between 1 to 40 bases can be produced.

Incorporation of artificial nucleotides, with modifications ranging from single atom exchanges, 5-I-dCTP, 7-deaza-I-dATP, 5-Br-dUTP and 6-S-dGTP,

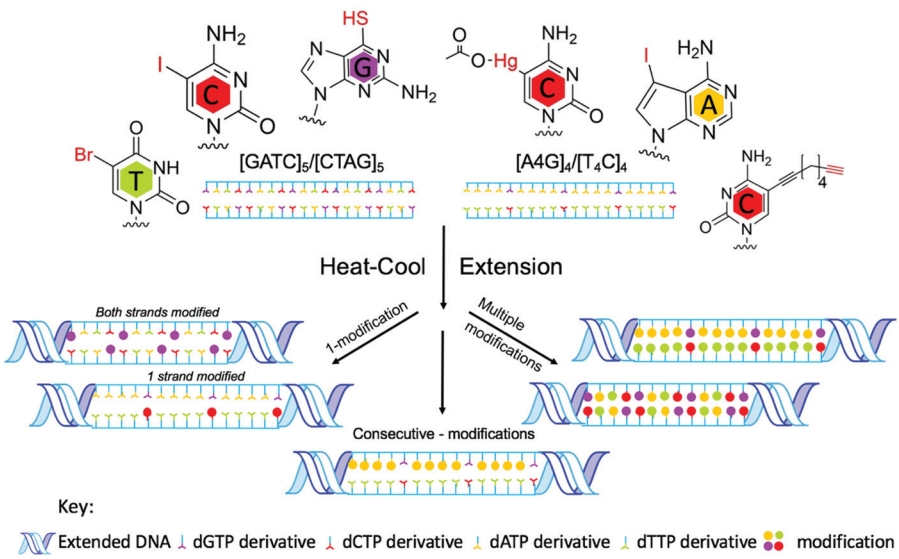

Figure 1 DNA extension by heat-cool cycles to produce modified DNA with singular or multiple modifications on one or both strands.

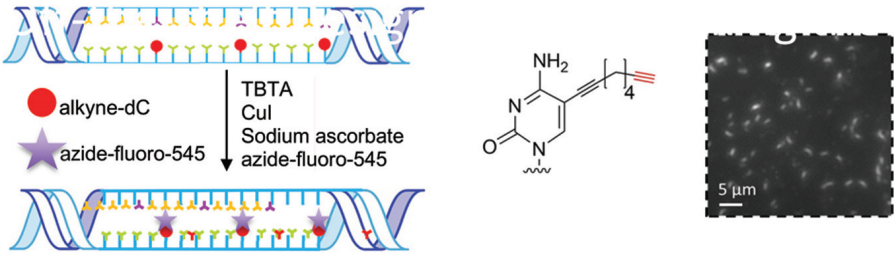

Figure 2 Click modification of alkyne-dC bearing DNA with an azido-flurophore.

to long chains, 5-C_8-alkyne-dCTP, was demonstrated. Modifications situated in the major groove have little effect on the DNA polymerase efficiency but reduced enzymatic processivity is observed if the modification lies in the hydrogen-bonding region. By tailoring the oligo-seed, it is possible to synthesise long designer DNA to include modifications at user-defined positions. The modified DNA product lengths are similar to the unmodified DNA products, except for 6-S-dGTP, which yielded DNA of 500 base pairs.

6-S-dGTP is renowned for strong metal interactions, and was exploited for the specific localisation of Au^{+}, Ni^{2+}, Cd^{2+} and Au^{3+} at repeating G positions. As the final 6-S-DNA product is limited in length, an alternative thiol modification was investigated. Using phosphorothioate dNTPs, sulfur bearing DNA products similar in length to the unmodified DNA were produced after 30 heat-cool cycles. This enabled the specific positioning of Au-nanoparticles through careful oligo-seed design.

DNA bearing the 5-C_8-alkyne-dCTP provides alkyne anchors at sites sitting in the major groove. To demonstrate the ability to add a second layer of design, click chemistry with azide-fluor-545 was investigated. This opens up potential routes to more complex modifications via organic synthesis at precise sites within the designer DNA.

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15:15 – 15:35

Towards Artificial Synapses: Nanowire Memristor with Internal Resistance States

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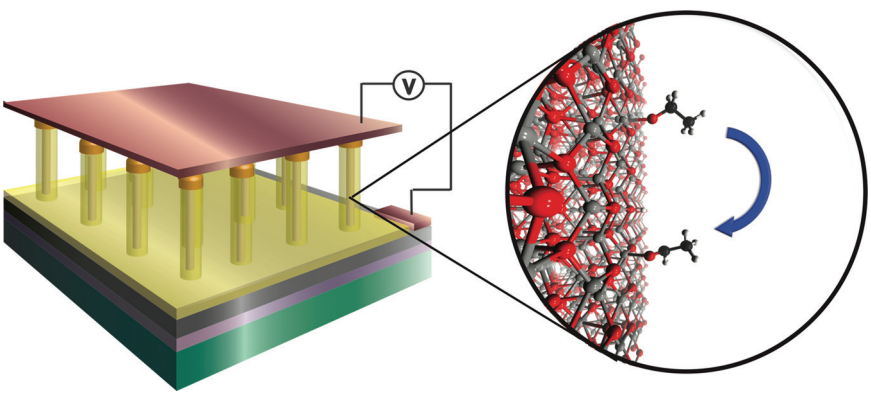
Synaptic plasticity is globally recognized as the key mechanism in higher brain functions such as learning and memory. Memristive devices are among the most promising candidates to emulate synapses in artificial neural systems, owing to their expected analog memory functionality, as well as their inherent attitude to downscaling. This scientific breakthrough is currently limited by intrinsic digital nature of the resistive switching mechanism, so that the implementation of memory and learning rules can be accomplished only by introducing complex external engineering of electrical signals. All solutions to achieve multi-state devices proposed in literature require external artificial resources: tuning the compliance current and/or the maximum applied voltage, engineering the duration or amplitude of electrical pulses, implementing optimized training processes. Here we demonstrate, on the base of a combined theoretical and experimental investigation, that core-shell structures based on polymer-coated ZnO nanowires (NWs) exhibit a resistive switching behavior characterized by internal multiple resistance states, owing to resistive changes



induced by redox reaction occurring at the surface. We first prove the possibility of achieving multi-state NW resistivity by showing, by means of density functional theory (DFT) calculations, how the electronic properties of ZnO surfaces changes when interacting with the typical organic functional groups present in polymers. Subsequently an experimental realization of a memristor device based on arrays of ZnO NWs is presented, exploiting the mechanism discussed theoretically. This memrisistive device can bridge the gap with the needs of incremental learning rules, thus paving the way to a new generation of artificial neural systems.

15:35 – 16:15

Ion-Gated Single Molecular Junction: Chemical and Electrochemical Approach

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The assembly and implementation of organic molecules in electronic circuits represents an inspiring alternative to silicon based technology for further miniaturization. Although a substantial progress has been made toward the ultimate goal, there are several obstacles mainly concerning the techniques for measuring and tuning the charge transport through the molecules. These barriers are more drastic when the charge measurement and regulation comes to the level of single molecules. At the sub-nanometer size of the single molecules, the well-defined measurement of electrical characteristics is of high challenging issue. For this purpose, "break junction" techniques have been developed aiming at answering the questions about the effect of interface, junction geometry, the environment surrounding the junction, molecular structure, and so on. Furthermore, a modified break junction setup can be used for tuning the charge transport through the junction. A state of the art concept for this is "(Electro)chemical or ion gating" control of the conductance.

Electrochemical gating control of a single molecule can be performed employing "scanning tunneling microscopy-break Junction (EC-STM-BJ) and we found the applied electrochemical gate potential is able to tune the charge transport properties of different redox active/inactive system in an electrified gold/electrolyte interface. Scanning the sample potential versus the reference electrode like in an electrochemical with the fixed bias potential can change the relative position of the frontier molecular orbital to the Fermi level of the electrodes and depending on the molecular properties, several phenomena can be observed [1–3]. Figure 1 shows the experimental setup for an EC-STM-BJ instrument.

Similar to electrochemical gating, ion gating approach can be applied to the single molecule conductance measurements to study the fundamental charge transport properties of a molecular system. Figure 2 shows different isomers of Borepin molecules. Depending on the location of the boron atom, different electron pathways in the conjugation network is likely. Single molecule charge

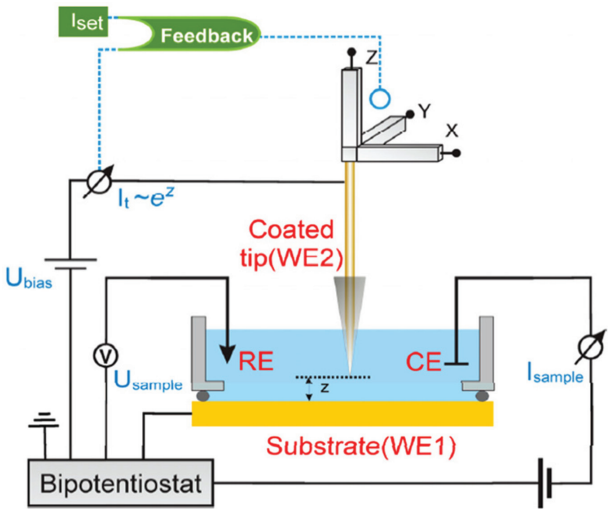

Figure 1 Demonstration of an EC-STM-BJ setup.

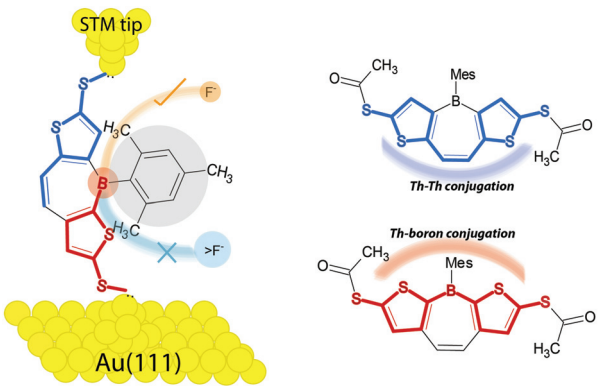

Figure 2 Borepin molecular structure with differerent electron pathways and fluoride offinity.

transport properties of the DTB isomers show a different behavior in the conductance as well as spectroscopic and redox property when boron atom is or is not involved in the charge transport channel in the junction. Furthermore, a significant change in the conductance response of the individual DTB isomers is found in the presence of specifically fluoride ion. The boron-fluoride coordination induces a switching of the conductance which varied widely among the isomers, consistent with the ensemble photophysical measurements indicating the uniqueness of electronics in the different systems [4].

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16:30 – 17:10

Electrochemically Modulated Electrical Properties of DNA Duplexes

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Highly specific interactions between DNA bases underlying the unique biorecognition and electronic properties of DNA allow their challenging bioelectronic and biosensor applications [1]. In particular, DNA sensing technologies, exploiting differences in electrochemical properties of single stranded (ss) and double stranded (ds) DNA, provide efficient tools for genetic analysis based on DNA hybridization [2]. Discrimination between ssDNA and dsDNA is then performed either through the reactions of DNA with redox indicators, capable of specific interactions with ss or dsDNAs [3], or via variations of the electrochemical signal stemming from the electrode-tethered redox-labelled DNA [4], both strongly depending on electron transfer (ET) properties of individual DNA molecules.

Here, I overview our recent studies of ET mediated by the DNA duplex, operating as a one-dimensional electronic conductor [5, 6], and of ET in the redox probe-conjugated DNA duplexes triggered by the potential-induced diffusion of the redox probe to the electrode [7, 8], including the ways of their optimisation by the proper choice of the DNA probes [5, 9], removal of the alkanethiol linker representing an extra barrier for ET and introduction of new "minimized" linkers [6]. These results allow better understanding of ET reactions proceeding in the electrode-tethered DNA and assist the design of advanced biosensor technologies for single nucleotide polymorphism.

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17:10 – 17:30

Highly Biospecific Self-Assembled Aptasensors for Dopamine Analysis

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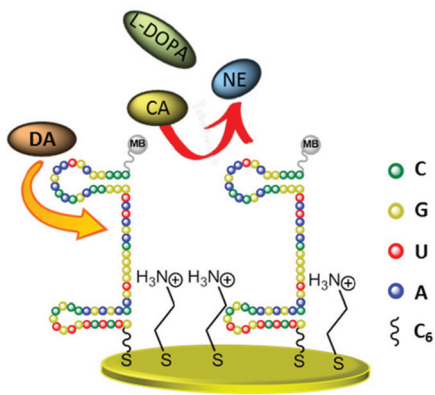
In order to investigate the role of small molecule neurotransmitters in the complex landscape of brain inter-neuronal communication, and ultimately, to relate this information to complex behavior and brain disorders, **chemically specific *in vivo* sensors** are required. That is particularly true in the electroanalysis of dopamine, which oxidation potential usually overlaps with other coexisting neurotransmitters and interfering species. To tackle the problem of low specificity, aptamers (*i.e.*, nucleic acid sequences able to specifically recognize and bind certain ligands) have been coupled with electrochemical detection. This approach has allowed sensitive, simple, and cost-effective electrochemical sensing of small molecules such as cocaine [1] or adenosine [2] by DNA-aptasensors and theophylline [3] or dopamine [4] by RNA-aptasensors.



Here we report a **highly biospecific self-assembled aptasensor for electroanalysis of dopamine**. Capture surfaces have been designed so that tethered RNA aptamer strands had enough conformational freedom for target binding beyond a dense monolayer of cysteamine to minimize nonspecific

binding [5]. We have demonstrated that these surfaces selectively recognize dopamine in the presence of structurally related neurotransmitters, such as catechol, norepinephrine or L-DOPA, and such co-existing interferents as ascorbic and uric acid [4]. One of our main goals was to probe that even though RNA aptamer stability can be compromised in biological fluids by the ribonuclease digestion or chemical cleavage [6], binding to electrodes stabilize their structure, so that measurements can be performed in undiluted biological fluids (i.e., human serum and blood). Therefore, this sensing platform provides a reliable and specific methodology for *in vivo* screening of dopamine levels that could be used in drug-administered Parkinson's patients' blood plasma and serum. Ultimately, it will enable the development of miniaturized devices that will advance the understanding of neuronal circuits uncovering processes associated with cognition, emotion, learning and memory.

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17:30 – 17:50

Thin-Film Nanocrystalline Diamond Electrodes for Neural Stimulation Applications

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Nanocrystalline diamond (NCD) films have emerged during recent years as promising coatings for biomedical devices thanks to their many outstanding physical and chemical properties [1]. In particular, boron-doped diamond NCD films possess excellent electrochemical properties, which have raised interest for their application in the fabrication of neural electrodes. Here, a series of studies evaluating the biocompatibility and electrochemical performance of thin-film NCD electrodes are presented. NCD films were synthesized by means of microwave chemical vapor deposition on the surface of various test substrates and neural electrodes. The samples were assessed by different surface characterization methods, including Raman spectroscopy, AFM and SEM. The *in vitro* biological performance of the NCD films was investigated by means of protein adsorption, cytotoxicity, and cell proliferation assays. *In vivo* studies comprised biocompatibility and electrochemical measurements after subcutaneous implantation of the electrodes in rats. Apart form demonstrating that NCD films are not cytotoxic, cell culture studies have shown that among the different surface properties, roughness of the NCD films plays a significant role in modulating protein adsorption and cell adhesion [2]. Data from electrode implantation studies revealed that boron doped NCD films are associated with no signs of chronic inflammation and a very thin fibrous capsule [3]. *In vitro* electrochemical performance studies of boron doped NCD electrodes demonstrated that parameters such as impedance and charge injection capacity are similar to conventional titanium nitride (TiN) electrodes, but NCD electrodes display a much wider water potential window, ranging from –1.7 to 1.4 V. *In vivo*, immediately upon implantation, boron doped NCD electrodes displayed a decrease in the VTs and an increase in the pulsing capacitances, which remained stable throughout the whole implantation period, whereas the opposite was the case for the TiN electrodes [4]. These results revealed that boron doped diamond electrodes possess a superior biofouling

resistance, which provides significantly stable electrochemical properties both in protein solution as well as *in vivo* [4]. Finally, we show that the charge storage and charge injection capacity of diamond thin-film electrodes can be significantly enhanced by synthesizing the films on porous TiN electrodes [5].

In summary, our data demonstrates that boron doped NCD electrodes display reduced biofouling by proteins, cause a minimal foreign body reaction upon implantation, and can be safely operated within a wide potential window. Furthermore, we show that increased porosity can significantly boost the charge injection capacity of NCD electrodes, making this material well suited for neural stimulation applications. Taken together, these results indicate that boron doped NCD films represent a promising approach for the development of the next generation of neural stimulation electrodes.

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18:00 – 18:20

Aromatic Side-Chain Exciton Coupling Sheds Light on Antimicrobial Peptide Self-Assembly

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The development of antibiotics was a giant breakthrough for humankind. However, the steadily growing antimicrobial resistance is increasingly hindering treatment of bacterial, viral, fungal and parasitic infections [1]. It is therefore foreseen by the scientific community [2] that this rise of antibiotic resistance will have major repercussions on the life quality of future patients and their families, with no real solution being currently available. The number of affected people in the world is expected to increase in coming years, demanding a response from public health systems [3]. However, as the healthcare costs associated to this type of infections are high, this also results in an economic challenge for the countries involved.

Gram-negative bacteria are generally considered more harmful than the gram-positive, mainly because of a different composition of the outer membrane [4, 5]. For example, gram-negative bacteria exhibit a reduced susceptibility to penicillin and they possess endotoxic lipopolysaccharide in their outer membrane [6].

Striving towards the discovery of novel antimicrobial drugs, a very promising avenue to pursue is the development of antimicrobial peptides (AMPs) [7]. Cationic AMPs are particularly suitable to target the anionic lipid-rich membrane of gram-negative bacteria and disrupt the cytoplasmic membrane. As to counter membrane disruption, bacteria would have to significantly modify their membrane composition, antibiotic resistance mechanisms are not likely to emerge in a short timeframe.

Even though, to a certain extent, the antibiotic mechanism of AMPs is known [8], more efforts are needed to improve our understanding of such promising systems and increase their efficacy.

In this work, we employ synchrotron circular dichroism (SRCD) to obtain insights about AMPs folding dynamics. In addition to the typical secondary structure signatures emerging from the analysis of CD spectra arising from the peptide bond absorption in the far-UV, exciton coupling [9], originated from aromatic side-chains, is considered. Conventional analysis of CD spectra neglects the contribution of the side-chains by observing only the asymmetrical features of the peptide backbone. In this work, we aim at progressing beyond the analysis of peptide bond as sole chromophore by introducing aromatic side-chains as additional chromophore and by observing their exciton coupling occurring in the far-UV.

Figure 1 offers a schematic overview of aromatic side-chain exciton coupling.

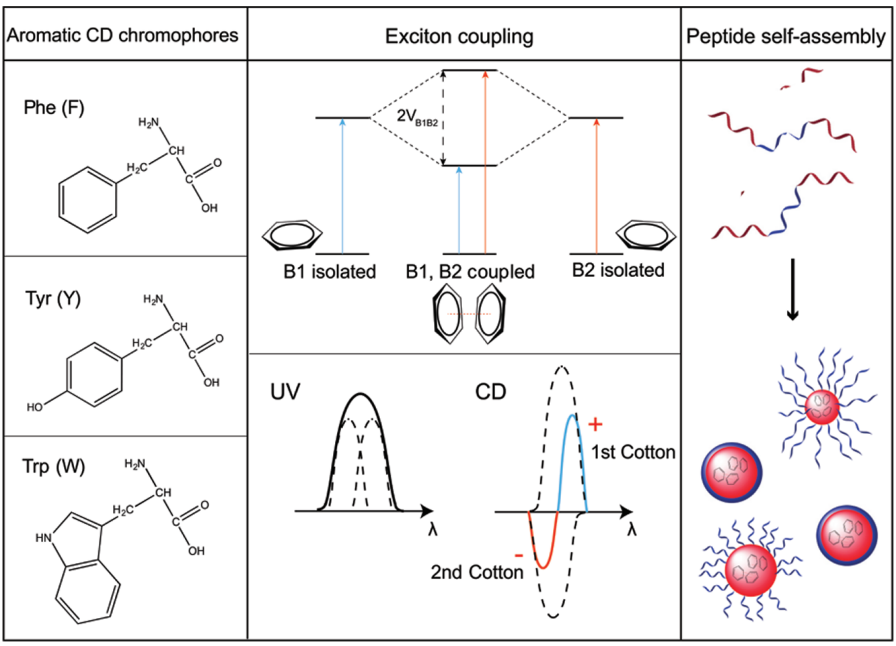

Figure 1 Schematic overview of aromatic side-chain exciton coupling. Left panel: aromatic residue molecular structure; transition properties of phenylalanine side-chain can be approximated as an alkylated benzene, tyrosine's as an alkylated phenol, tryptophan's as an indole. Centre panel: exciton coupling principle; if aromatic chromophores are brought close enough, coupling of their transition can occur. V_{B1B2} is the Davydov splitting [10, 11]. Right panel: model of amphiphilic cationic AMPs self-assembly in a polar solvent (e.g. DI water); in this example, segments in blue are positively charged residues (e.g. lysine, arginine), segments in red are hydrophobic regions where aromatic rings are close by so to allow exciton coupling to occur.

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18:20 – 19:00

Apertureless Near-Field Scanning Microscopy of Polymer Surfaces – Material Recognition

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We present physical principles of Apertureless Scanning Near-field Optical Microscopy (ASNOM) [1–3] and report on its application to a mapping of the nanoscale objects optical properties with nm-resolution.

Normally, the dipole oscillations in a point-like object (like a single molecule or nano-particle) can hardly be emitted into an environmental space as a running electromagnetic wave. Its dipole momentum determined by a few oscillating electrons (typically single one) and angstrom-range oscillation span of charge density yields in vanishingly low efficiency in a light emission. The situation changes dramatically if a rod-like antenna of some micrometer length is attacted "electrically" to that object (see Figure 1). A huge amount of free electrons in a metal of a tip being involved in the charge density oscillations under an influence of the object being investigated, as well as tip large dimensions lead to $10^4 - 10^5$ increase of radiation efficiency [4]. An external electromagnetic field can, vice versa, be applied to a surface with a help of an ASNOM tip. The dimensions of area where the field is applied are determined just by mechanical dimensions of a tip (5–20 nm) [5–7], regardless to the wavelength of a light being used (up to THz range).

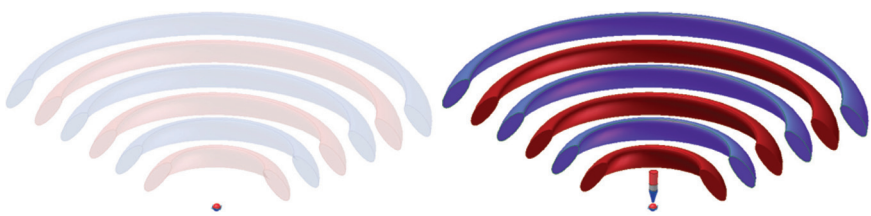

Figure 1 Light emission by a point-like nano-object without tip antenna (left) and in a presence of a tip (right).

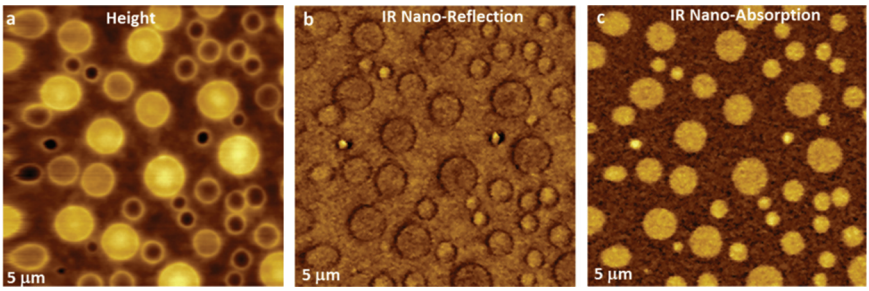

Figure 2 Polystyrene embedded in a PVAC matrix. (a) AFM-like topography map of the sample. ASNOM signal ($\lambda = 10.6$ µm) with (b) an optical phase corresponding to Au (known to perfectly reflect 10.6 µm radiation) and (c) collected with an optical phase 90° with respect to (b).

The amplitude and phase of the wave re-emitted by a tip antenna depend on its "grounding conditions", and therefore an ASNOM signal being collected contains information on the sample local dielectric function as a complex value [8].

We present ASNOM images of semiconductor and polymer (e.g. Figure 2) structures of nanometer scale to demonstrate an ability of an ASNOM to map a clear material contrast, with a lateral resolution of 10–30 nm.

We also present the maps of running surface polariton waves collected with an ASNOM on different samples. A nanometer lateral resolution of ASNOM allows for mapping the surface waves with a lateral resolution much better than a wavelength and, therefore, to investigate the polariton optics phenomena in such kind of structures with a rather good precision.

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18/11/2016

09:00 – 09:40

Functional and Responsive Core-Shell Nanoparticle Assembly at Oil and Lipid Interfaces

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Carefully controlled core-shell nanoparticles can be used in biomedical applications, e.g., as biomedical imaging contrast agents, for hyperthermia and in drug delivery [1, 2], as well as for biotechnological applications such as separation and purification. Unique material functions can be achieved by using nanoscale inorganic cores, such as plasmonic or superparamagnetic interactions with electromagnetic fields. However, to enable these functions in a biological environment a dense organic shell has to control colloidal interactions with biomolecules, cells and other nanoparticles [1, 3]. Control over nanoparticle physical properties through an organic shell also allows tailoring of the assembly of functional nanoparticles into supramolecular

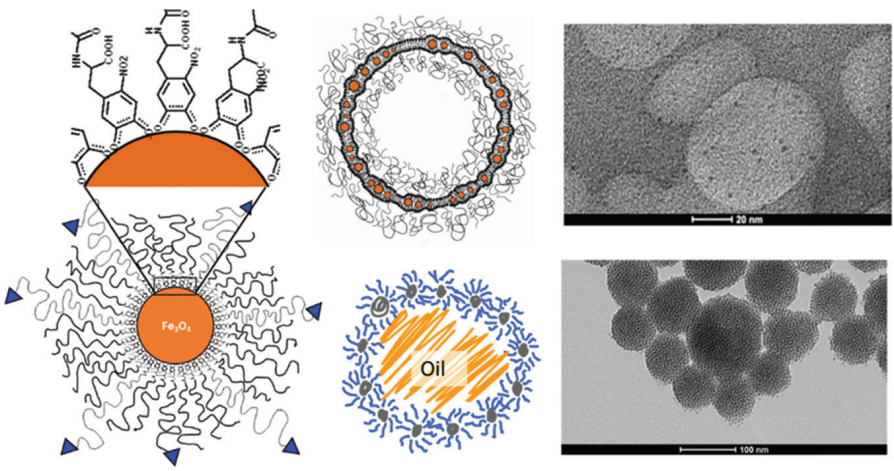

Figure 1 Left: Schematic of iron oxide – polymer brush core-shell nanoparticles, and magnetoliposomes and magnetic emulsomes assembled from core-shell nanoparticles. Right: TEM of self-assembled magnetoliposomes and core-shell nanoparticle stabilized emulsomes.

structures, such as nanoscale vesicles or nanoscale Pickering-type emulsomes. The self-assembled structures can incorporate environmentally responsive building blocks and therefore be controlled through the strong interaction of the inorganic core with externally applied electromagnetic fields.

I will describe multiple recent developments from our lab regarding the synthesis and assembly of superparamagnetic core-shell nanoparticles that illustrate this design philosophy. The combination of new organic shell grafting methods [3–7] and control over nanoscale self-assembly [8–13] has allowed us to vastly improve performance of superparamagnetic core-shell nanoparticles, perform detailed investigations of interactions of colloidal responsive nanoparticles as well as demonstrate unprecedented control over magnetically controlled nanovesicular and nanoemulsion systems for transport and release applications that could impact future directions in drug delivery and biomedical imaging.

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09:40 – 10:20

Microbial Extracellular Electron Exchange

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Extracellular electron conducting structures have been described for different bacterial species. Initially, bacterial 'nanowires' were observed in metal-reducing bacteria such as *Geobacter sulfurreducens* and *Shewanella oneidensis* and they were shown to mediate transfer of electrons from the cell surface over micrometer distances to extracellular electron acceptors or in long-range cell-cell networks in biofilms [1]. The *G. sulfurreducens* nanowires were shown to be type IV pilus-based and composed of a short version of the PilA subunit. Multiheme c-type cytochromes were also shown to be important for extracellular electron transport [2]. Cable bacteria recently revealed a novel extracellular electron transfer route [3, 4]. They are a radically different form of life and forms centimeters-long filamentous, multicellular organisms conducting electrons from one end to the other. This is apparently achieved through outer-membrane associated longitudinal strings ('biowires') that connects all cells of the bacterial filament. Preliminary modeling indicates a conductivity orders of magnitude higher than any other biological material, and even competitive to doped synthetic polymers currently used in organic electronics.

We are employing structural and functional methods to unravel the mechanistic details of these intriguing bioelectrical wires at the molecular level with

the ultimate goal to obtain an understanding of the underlying supramolecular organization and conduction mechanism and the status for this work will be presented.

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10:35 – 11:15

Enhancement of Two-Photon Photoluminescence and SERS for Low-Coverage Gold Films

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Electromagnetic field enhancement effects occurring in thin gold films are investigated with two-photon photoluminescence (TPL) and Raman scanning optical microscopies [1]. Gold films with nominal thicknesses of 3, 6, 8, 10, and 12 nm are fabricated using electron-beam deposition with a rate of 2 Å/s onto room-temperature glass substrates. The samples are characterized using scanning electron microscopy (SEM) images, from which we infer

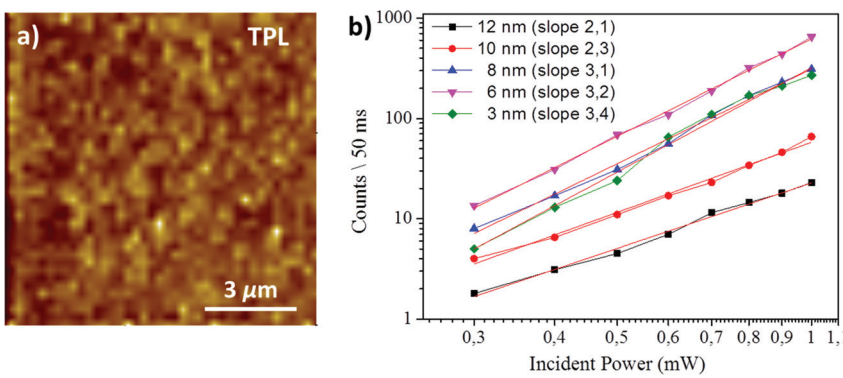

Figure 1 a) Typical TPL image from the thin gold films, obtained here for 6 nm thickness (Signal levels at bright spots are typically larger by 30–40%, than the average TPL signal). b) Dependence of TPL signal on the power for the thicknesses 3, 6, 8, 10, and 12 nm. The log/log curves are shown with a linear curve fit and slope-values in the legend illustrate the super-cubic signal dependence on incident power [1].

that the 6-nm-thin film is very close to the percolation threshold, and linear optical spectroscopy. TPL images obtained with the incident radiation in near infrared (730–860 nm) exhibit a strong increase in the level of TPL signals for film thicknesses near the percolation threshold. For some thicknesses, TPL measurements reveal super-cubic dependences on the incident power rather than the expected (and usually observed) quadratic dependence. We ascribe this feature to the occurrence of very strongly localized and enhanced electromagnetic fields due to multiple light scattering in random nanostructures that might eventually lead to white-light generation involving various high-order nonlinear processes [2, 3].

For Raman microscopy characterization, the samples were covered with a Crystal Violet dye. Raman images obtained at the pump wavelength of 532 nm exhibit significant increases in Raman signals when decreasing the film thickness from 12 to 6 nm. At the same time, noticeably lower signals are observed with the 3-nm-thin (island-like) film as compared to the 6-nm-thin film, a feature that correlates well with the TPL observations indicating that highest field enhancements are to be expected near the percolation threshold. In the light of [4] we speculate that the high FE and the nonlinear response could be associated with nonlocal dynamics.

The results obtained with TPL and Raman measurements demonstrate that easy-to-fabricate and scalable semi-continuous metal films constitute a viable approach to design of substrates needed for surface-enhanced spectroscopies

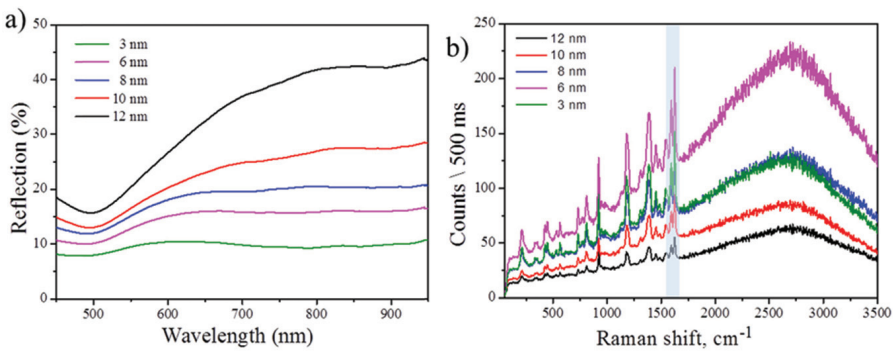

Figure 2 a) Reflection spectra obtained for the thin gold films with nominal thicknesses of 3 nm, 6 nm, 8 nm, 10 nm, and 12 nm and normalized to a reference spectrum recorded from a bulk optically-smooth gold surface. b) SERS spectra of Crystal Violet with concentration 10^{-6} M for all thicknesses (3, 6, 8, 10, and 12 nm) [1].

in various (for example, sensing) applications. The possibility for supercontinuum white-light generation in the percolation geometry should be investigated further, using also spectral and time-resolved measurements.

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11:15 – 11:55

Metal Nanostructures for Light-Trapping in Thin-Film Solar Cells and Waveguides

Thomas Søndergaard*, Yao-Chung Tsao, Peter K. Kristensen, Thomas G. Pedersen and Kjeld Pedersen

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A key approach for improving thin-film solar cells is to make use of light-trapping in the active layer. This can be achieved by structuring the solar cell either on the front surface, on the back-reflector, or by embedding scattering particles. Without such structuring, the part of the incident light with wavelengths near the solar cell bandgap, and consequently with weak absorption in the solar cell, will either propagate straight through the solar, or in the case of a back-reflector, the incident light will be mainly reflected out of the solar cell, and in both cases with little absorption. By appropriate structuring of the solar cell the result will be scattering or diffraction of incident light into directions in thin-film solar cells, where the mechanism of total-internal reflection will make the light be trapped and propagate a longer distance inside the active layer. Especially for wavelengths near the solar cell bandgap, where absorption of light is weak, the longer propagation distance will lead to increased absorption and thus improved conversion efficiency. The thin active layer (silicon) of the solar cell can be thought of as a waveguide for light, and in that view the light-trapping takes place by coupling of light into guided modes of the waveguide.

In this talk we will report on mainly two of our efforts concerning light-trapping nanostructures. The first one is concerned with obtaining a structured back reflector using anodized aluminum (see e.g. [1]). By applying an appropriate acid, a voltage, and by appropriate temperature control, an aluminum foil can be nanostructured with a roughly hexagonal pattern having various periods and with some disorder. By depositing the rest of a solar cell on top the structured aluminum surface will function as a back-reflector giving rise to trapping of incident light in the solar cell active material. We have also considered texturing of the front surface of the solar cell with scatterers having a large distance between them [2]. The large distance was chosen to study the effect of a single scatterer. In the case of metal scatterers they may

have resonances related to localized plasmons. However, the main finding is that strong scattering is dominated by properties of the solar cell waveguide geometry. Thus, strong scattering is observed near those wavelengths where the waveguide geometry has a cut-off of a guided mode. Thus, a main result is that focus should not only be on the resonances of individual metal scatterers, but it should also be on resonances related to the waveguide geometry. Most of the work that will be reported in this talk was carried out in the project THINC (thin-film solar cell based on nanocrystalline silicon and structured backside reflectors).

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12:40 – 13:20

Construction of Organized Materials through Self-Assembly of Protein Fibrils

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Biologically derived materials often display hierarchical organization of nano-structures, lending unique properties to the macroscopic material. In this contribution will be discussed how to prepare hierarchically ordered materials based on functionalized protein nano-fibrils (amyloid-like fibrils). Protein fibrils can readily be prepared by heating of acidic protein solutions. By proper choice of reactions conditions these structures can then in turn be induced to assemble into hierarchically organized macroscopic structures. We have developed novel techniques for preparation of functionalized protein

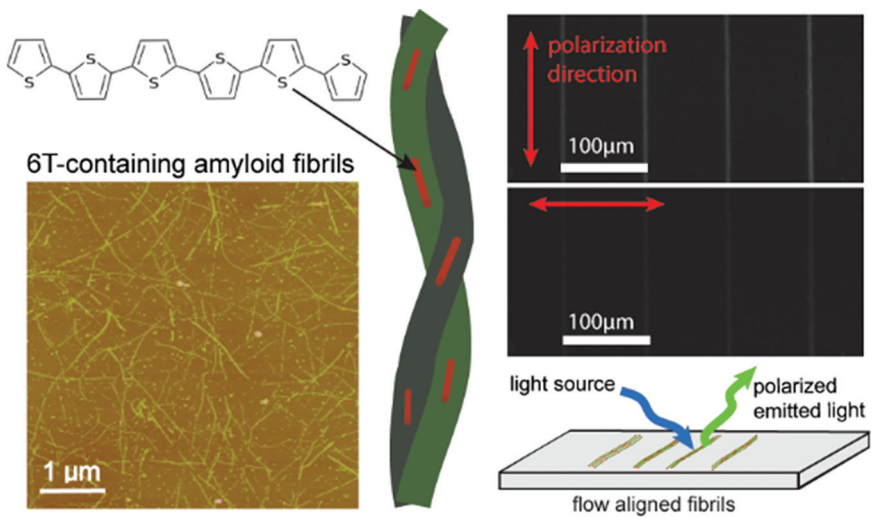

Figure 1 AFM image of functionalized amyloid fibrils complemented with a schematic drawing of a fibrils incorporating 6T molecules (a fluorescent dye). Because of the fine structure of amyloid fibrils the 6T molecules become oriented along the long fibril axis. The fibrils can in turn be aligned by flow, resulting in protein stripes exhibiting emission of polarized light [3].

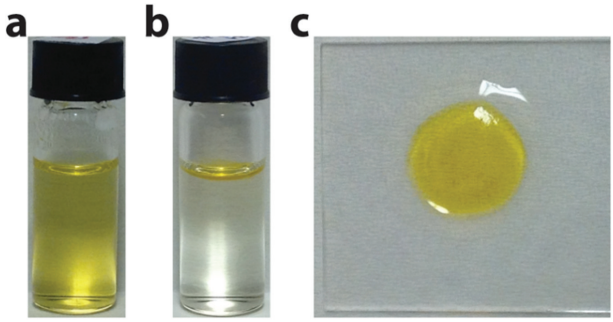

Figure 2 Illustration of convection induced self-assembly of functionalised protein fibrils. a) A dispersion of protein fibrils functionalized with a yellow dye. b) The same dispersion after film formation through self-assembly. c) The film transferred to a glass-slide.

materials. One extremely flexible and facile method involves co-grinding of a protein with a hydrophobic material. Upon exposure to appropriate stimuli the composite undergoes self-assembly into functionalized fibrils [1–3]. These fibrils can in turn be hierarchically organized into films displaying anisotropic optical properties [1–3] (Figure 1). In addition, free standing films can be formed by convection induced self-assembly (Figure 2). Protein fibrils can be functionalized with conductive polyelectrolytes, resulting in conductive nanowires [4]. In conclusion a wide range of functionalized protein structures can be prepared displaying a variety of properties such as emission of polarized light or electrical conductivity.

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13:20 – 14:00

Multiscale Design and Synthesis of Porous Nanostructured Materials

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It has become increasingly clear that hydrogen as a viable energy carrier may play an important role in future energy plans. However, development of reasonably safe and reversible hydrogen storage materials for transportation is still a great challenge. In this work, we present the scheme of designing novel materials and address the multiscale simulation method, in which the first-principles calculation is performed to calculate the interaction energy between adsorbate and adsorbent, and then the interaction is input to grand canonical Monte Carlo (GCMC) simulation for evaluation of hydrogen storage capacities [1, 2]. By using the multiscale simulation method proposed, a series of novel materials are designed by simulating synthesis. These materials include new carbon allotrope – diamondyne [3], porous organic polymers [4], Li-doped covalent organic frameworks (COFs) [1], porous aromatic frameworks (PAFs) [5]. Furthermore, hydrogen storage capacities of these materials are also investigated. Although all these materials show excellent hydrogen storage properties, modification of these materials can further improve their hydrogen storage capacities. Toward this end, we also used the multiscale simulation method to screen the metal dopants to modify these materials, and found that the lithium atom is the best modifier of COF materials for enhancing gas storage. More importantly, we also used experiments to synthesize the designed materials to confirm the multiscale simulation results [6]. Besides hydrogen storage materials, we also investigated the nitrogen-doped graphene analogue materials for oxygen reduce reaction [7–9].

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14:00 – 14:20

Effect of a Dual Charge on the DNA-Conjugated Redox Probe on DNA Sensing by Short Hairpin Beacons Tethered to Gold Electrodes

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Differently charged redox species can differently affect the interfacial behavior of biomolecules, particularly, the electrochemical behavior of DNA-conjugated species [1, 2]. Finer tuning of the electrochemical response can be achieved by varying either the nature of the redox molecules conjugated to the surface-tethered DNA or the charge of the electrode. Here, it is shown that the sensitivity of genosensors based on methylene-blue (MB) labelled hairpin DNA structures tethered to gold electrodes and the mechanism of electron transfer (ET) between the redox label conjugated to double stranded (ds) DNA and the electrode depends on the overall charge of the MB molecule [3].

The positive charge on MB promotes attractive electrostatic interactions between MB and dsDNA, leading to MB binding to the duplex, in which case MB electrochemistry will be substantiated by ET mediation by DNA. On the other hand, when MB bears an additional carboxylic group providing an extra negative charge on the MB molecule which impedes close interactions between MB-COOH and DNA, thus the ET is limited by diffusion of

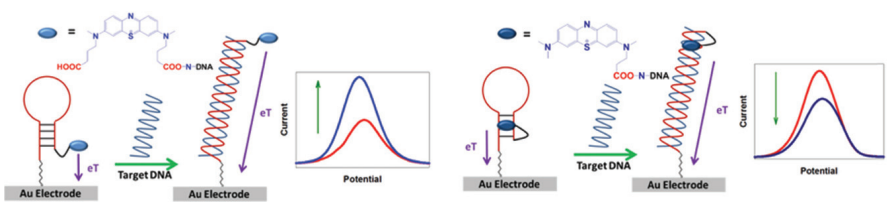

Figure 1 Schematic representation of the MB-labeled DNA hairpin beacons tethered to gold electrode and chemical structures of the corresponding MB labels.

MB-conjugated dsDNA to the electrode surface. It appears that, the absence or the presence of this extra COOH group is responsible for the different patterns of the hairpin beacon operation. It also affects, both the electroanalytical performance of the genosensor changing the ill-defined "off-on" pattern, detectable only at μM levels of analyzed DNA and the robustness of the DNA analysis, especially in the nM DNA range [3].

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14:35 – 15:15

Nanoscale Gymnastics: Dynamics of Protein-DNA Complexes with High Speed AFM

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A low data acquisition rate of AFM is a serious deficiency if AFM is applied to imaging of the majority of biological processes. For example, the translocation of RNA polymerase along DNA occurs on the second time scale, therefore the observation on the minute time scale reveals only few percent of the events. The high-speed AFM (HS-AFM) instrument developed by T. Ando operates with the sub-second image acquisition speed [1]. Key issues for high-speed AFM realized in the Ando design are as follows (1) small cantilevers with a resonant frequency above several hundred kHz and a small spring constant, (2) a high-speed scanner with a resonant frequency that matched the cantilever characteristics, (3) active damping techniques to suppress mechanical vibrations of the scanner, (4) fast feedback control and (5) gentle touch of the sample – the current HS-AFM instrument can capture images with the video rate without significant disturbance of weak biomolecular interactions [1, 2]. In this talk, I review results of HS-AFM applications to a number of protein-DNA complexes. They included direct visualization of interaction with DNA SSB protein that binds to single-stranded segments of DNA only [3]; visualization of dynamics of APOBEC3G protein in its interaction with the cognate site within DNA [4]; discovery of spontaneous unwrapping of nucleosomes [2]; observation of the long-range sliding of synaptosome along DNA [5] and visualization and analysis of concerted cleavage by type IIF restriction enzyme SfiI [6]. Prospects for the future applications of HS-AFM to biological systems will be discussed.

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15:15 – 15:35

Electrochemical Assay for a Total Cellulase Activity Using Thin Layer Nitrocellulose Modified Graphite Electrode

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In this paper, we report a simple and efficient assay for the total activity of cellulase using an electrochemical method. This assay employs nitrocellulose as a substrate, wet cast on flattened graphite electrode, creating an insulating nitrocellulose thin film where ferricyanide electrochemistry as redox indicator, is totally inhibited. The signal is gained after the exposure of cellulase, where it hydrolyze β-1-4-glycosidic bonds of nitrocellulose, creating crack and holes in the thin film and exposing naked graphite electrode surface, allowing ferricyanide faradaic signal. The changes of signals from

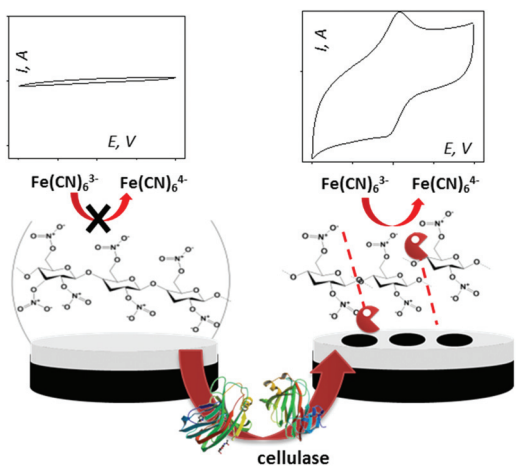

Figure 1 Schematic representation of the electrochemical assay for cellulase activity. A nitrocellulose insulating film is formed on the electrode surface, and ferricyanide electrochemistry is inhibited on such surface. Cellulase cleaves the glycosidic bonds in the film, and the electrode surface becomes exposed to the electrochemical reaction.

ferricyanide then correlated with the time of cellulase exposure where rates of cellulase reaction towards nitrocellulose are calculated. Not only has improved sensitivity $10^3 - 10^4$ folds compare to a standard method, this assay also shown to be able to distinguish type of cellulase, where it makes this electrochemical assay as the most perspective alternative method for research and industrial applications.

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Electrochemistry of Covalently-Linked Hemin/G-Quadruplex DNAzymes and its Applications in DNA Sensing

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Complexes of guanine quadruplexes (G4) with hemin is known to exhibit a peroxidase activity superior to that of pure hemin and thus are often referred to as a peroxidase-mimicking DNAzyme [1]. DNAzymes are often considered as more stable than natural enzymes, under certain conditions, and are easy to synthesize and modify. Therefore, they have been regarded as promising probes for bioanalysis. In the case of hemine-G4 complexes, they can be considered as a promising redox label for genetic electroanalytical platforms, which may allow accessible and inexpensive, and still sensitive and selective genetic analysis [2]. The main disadvantage of such assays is the insufficient stability of the non-covalent complexes of hemin and G4.

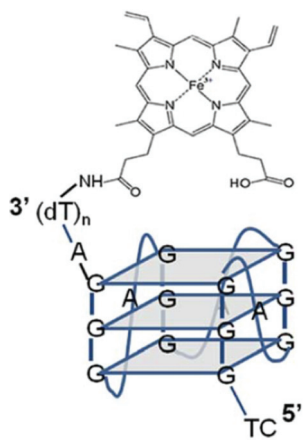

Figure 1 Schematic structure of the covalently-linked Hemin/G-quadruplex DNAzymes.

In this work, we report electrochemical studies of the covalent complexes of hemin-G4 produced by peptide-bond conjugation of hemin to amine-terminated G4-containing DNA sequences (Figure 1) [3] and use these covalent complexes, with non-dissociating hemin, in electrochemical DNA sandwich assay on magnetics beads. The results are compared with a previously reported electrochemical sandwich assays using enzymes as catalytic labels [4].

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Architecture Mutations + Contemporary Art – About Robotics, Cyborgs and NanoBiology: The Robot as a Factor in Contemporary Mutations

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In this research paper we report that we focus on the relationships that can be established between bio technological progress (more particularly in nano bio technology and robotics) and architectural processes. In this context, these approaches are fundamental into my research in the analysis of nano biological problems and context at different levels.

(title) "Development and creative processes of augmented intelligence organisms from smarts materials. Relationships of creation processes between architecture and nano-bio-robotics."

In this context we have observed, experimented and measured (unpublished yet but partially resolved at 70% (2.1/3) on July 21st 2013 in Amsterdam with help of a Physician from F.U Berlin, Masters Graduated in Applied Experimental Physics, specialist in f.e Adsorption properties of molecular switches at surfaces) that of so-called "smart materials." Issues in nanotechnology, mainly in nanobiorobotics, this type of intelligent organisms that are capable of interacting with their environment, change colour or even shape or repair themselves in a process called "augmented intelligence," are beginning to interact with the contemporary architectural world and deserve a definitive place in research.

However we could describe coming from the "biomimetic" 1 and "hybrid" 2 they are already used in medical research to eliminate cancer, infections, ageing or in the production of synthetic food. In an era revolutionized by the "medicalization of society" (Lipovestky) we can't help but wonder about our status as human beings and beings-in-the-world.

You can see as an example, among many others describes, the project Genetics Barcelona, in which trees are genetically created to clarify the cities, enlightening, through the creation of new forms of artificial dew, made possible by the smart materials as well as by the use of the GFP protein produced by the illumination of certain jellyfish. This work wants to reveal the world of large-scale manipulation in smaller structures and elementary, nanotechnology, genetics and architecture.

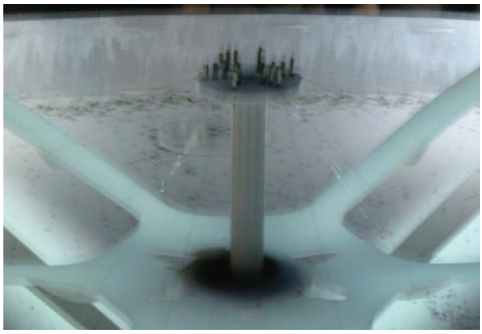

Figure 1 The Tragedy of the Commons.

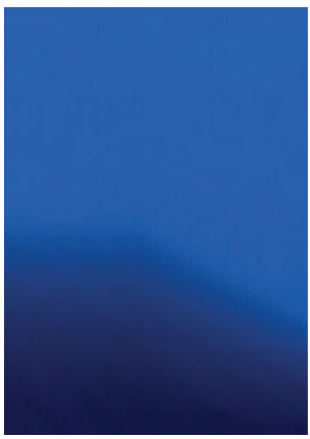

Figure 2 The Marble City Project.

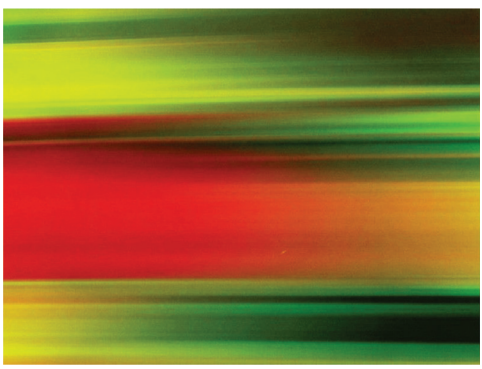

Figure 3 Heklugos.

Methods

Experimental, Applied Quantum Mechanics at nano scale.

From end 2009 to beginning 2014: Experimental applied approach and solution to a constructivist/deconstructivist quantum architecture approach, visual arts (sculpture, installation) and cinema, at nano scale. Creation processes in applied Art/Architecture at nano level using applied quantum mechanics experimental methods as concrete tangible solution for creation.

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