Self Assembly and Molecular Electronics

November 13–16, 2018, Aalborg, Denmark

ISBN: 978-87-7022-056-9 (Ebook)



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Functional Electrospun Phospholipid Nano-microfibers

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Drug Delivery to the Brain: How to Overcome the Blood–Brain Barrier?

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New Nanoscale Polymer Systems and their Interaction with Living Objects

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Suzhi Li

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Ye Tao *Rowland Institute at Harvard, USA*

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Duncan S. Sutherland *Aarhus University, Denmark*

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13:00 - 13:45

Design of (Thermo)Responsive Polymer-Grafted Nanoparticles for Biological Applications

Erik Reimhult

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Nanoparticles grafted with polymers are used and developed for a multitude of biomedical and biotechnological applications (Figure 1), such as imaging contrast agents, hyperthermia treatment drug delivery, separation and purification [1, 2]. Unique functions can be achieved for these applications by using nanoscale inorganic cores, such as nanoplasmonic metal cores or superparamagnetic oxide cores. However, the grafted polymer shell must prevent undesired colloidal interactions with biomolecules and cells that lead to aggregation and clearance to enable these functions in a biological environment; it also must promote desired specific biological interactions such as molecular and cellular targeting [1]. It is widely recognized that one of the best ways to achieve this is through grafting of the core particle with a dense brush of hydrophilic polymer, e.g. poly(ethylene glycol), which prevents protein and other biomolecules from binding to the particle and provides a scaffold for controlled functionalization with biofunctional ligands.

We will present our recent work on the design of monodisperse superparamagnetic iron oxide nanoparticles grafted with various sorts of polymer brushes. We will describe the influence of design parameters such as grafting [3, 4], polymer chemistry [5–8], core size [5, 9], molecular weight and polymer topology [10, 11] on nanoparticle performance. In particular, we will present recent results on protein interactions with such particles and the influence of the particle core on the specific avidity of ligands for biomolecular targeting [9, 12].

With increasing focus on multifunctional nanoparticles we have also studied how the morphology and topology of polymer shells influence the



Figure 1 Schematic of nanoparticle grafted with functionalized polymer brush.

colloidal and polymer solvation transitions of nanoparticles grafted with thermoresponsive polymer shells. We provide insight into how the high curvature of nanoparticle-grafted polymer brushes decouple colloidal and free polymer transitions as well as how physiological conditions greatly change the transitions of next-generation thermoresponsive polymer coatings for biomedical applications such as poly(2-alkyl-2-oxazolines) [10, 13, 14].

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13:45 - 14:30

Functional Electrospun Phospholipid Nano-microfibers

Ana C. Mendes and Ioannis S. Chronakis*

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Functional asolectin phospholipid nano-microfibers were developed using electrospinning processing with a range of fiber diameters and morphologies, depending on the phospholipid concentration and the solvent used [1, 2]. Chloroform and dimethylformamide, isooctane, cyclohexane and limonene



Figure 1 SEM images of electrospun asolectin solution using a single needle: (A) 45% w/w in CHCl3 : DMF [3 : 2 v/v], scale bar 20 μ m, (B) 50% w/w in cyclohexane, scale bar 20 μ , (C) 60% w/w in limonene, scale bar 100 μ , (D) 60% w/w in isooctane, scale bar 100 m μ . Inserts: histogram of the fiber diameter distribution.

were used as solvents. A critical concentration of phospholipids is essential to favor the intermolecular association between the micelles, required for the formation of asolectin electrospun fibers. The dielectric constant of the solvents had a strong influence on the electrospinning jet split properties and affected the morphology of the electrospun asolectin nano-microfibers, while co-axial electrospinning could be used to tune their average diameter. The mechanical properties and the stability at ambient conditions of phospholipid fibers were assessed by nanoindentation using Atomic Force Microscopy [2]. Their elastic modulus was found to be approximately 17.2 ± 1 MPa, and at a cycle of piezo expansion-retraction (loading-unloading) of a silicon tip on a fiber, a relatively high adhesion was observed during unloading. Moreover, the efficacy of electrospun phospholipid microfibers as antioxidants, encapsulation, and delivery matrices for bioactive compounds and transdermal drugs, were also confirmed [3, 4].

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14:50 - 15:35

Drug Delivery to the Brain: How to Overcome the Blood–Brain Barrier?

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Neurological diseases such as Alzheimer's disease and Parkinson Disease are becoming more prevalent worldwide. Unfortunately, treatment of neurological diseases is hindered by the inability of up to 98% of drugs with therapeutic relevance to cross the blood-brain barrier (BBB).

The blood-brain barrier (BBB) forms a chemical, physical and immunological barrier between the blood and the brain tissue. The BBB is formed by brain capillary endothelial cells (BCECs), which are interconnected by tight junctions, creating a tight seal between BCECs. Furthermore astrocytes and pericytes are situated in the near vicinity of the BCECs and helps strengthen the barrier properties of the BCECs.

In order to enhance drug delivery to the brain, different approaches have been developed. For decades, drug carriers like liposomes, antibodies and nanoparticles e.g. gold- or magnetic nanoparticles, have been investigated for the purpose of overcoming the restraints of the BBB. Which criteria the drug carriers should fulfill for the construction of an optimal design for overcoming the BBB are partly known, but many details are still to be discovered.

15:35 - 16:20

New Nanoscale Polymer Systems and their Interaction with Living Objects

M. I. Shtilman^{1,*}, A. N. Kuskov¹, P. P. Kulikov¹, A. L. Luss¹, A. V. Goryachaya¹, V. T. Dzhedzheya¹, S. A. Gusev², P. Henrich-Noack³, L. Gurevich⁴, V. P. Torchilin⁵, A. M. Tsatsakis⁶

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The synthesis methods and properties of amphiphilic polymers of N-vinylpyrrolidone, acrylamide, acrylic acid were studied and it was shown that these systems can be used for modification of liposomal membranes and as micelles-like aggregates [1, 2].

To the date, methods have been developed for the preparation of nanoparticles based on such polymers with immobilized poorly-soluble or insoluble in water low molecular weight, biologically active compounds, such as indomethacin, diclofenac, amphotericin B, nystatin, 5-fluorouracil, rifabutin, felodipine, ionol, curcumin. [3, 4].

On the other hand, aggregates of amphiphilic polymers of Nvinylpyrrolidone proved to be suitable for use as carriers of various proteins and peptides (blood factor IX, angiostatin, Bowman-Birk soybean proteinase (BBI). In this case, immobilization with the use of polymeric aggregates increases the resistance of proteins to denaturing effects, and thereof their total biological activity. Introduction of additional side amino groups in the polymeric part of amphiphilic systems allows the use of aggregates as carriers of nucleic acids and their subsequent application for transfection in genetic engineering [5, 6].

Using fluorescent labels and probes, it was shown that the immobilized substance introduced into larger size aggregates penetrates into the living cell due to endocytosis, localizing in the cytoplasm inside the endosome. On the other hand, when immobilized matter is introduced in smaller-size aggregates, it evenly spreads both in the cytoplasm of the cell and in its nucleus. When studying the transport of aggregates of amphiphilic polymers of N-vinylpyrrolidone in the body (rats), it was established that a fluorescent probe immobilized in aggregates of amphiphilic polymers, when injected into the tail of experimental animals, quickly reaches the vessels of the eye [7–9].

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16:20 - 17:05

Small-angle Scattering of X-rays and Neutrons as Structural Tools in Nanoscience: Block Copolymer Micelles, Protein-Detergent Complexes, Microgels and other Nanoparticles

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Small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) are excellent experimental tools for obtaining structural information on macromolecules, self-assembled structures, and nanoparticles in solution. The techniques give information on shape, size and organization of particles and molecules of sizes up to hundreds of nanometers with sub-nm resolution. It also provides key parameters such as mass, maximum diameter and radius of gyration. In contrast to many other techniques, SAXS and SANS does not require any special sample preparation or deuteration, and can be performed for almost any solvent/buffer condition, however, D₂O is usually used in the buffers for SANS as it enhances contrast and reduce background. Furthermore, the studied assemblies or particles may be amorphous or crystalline, may have disordered region or randomness, and may have (smaller) variation in size and shape without spoiling the possibility of structure determination. However, deriving detailed structural information from SAXS data requires sophisticated analysis approaches [1, 2]. There has been a large progress in analysis within the last decades and this has led to broad field of applications of the SAXS and SANS methods. In this lecture, the basic principles and



Figure 1 Examples of structures: Block copolymer micelles [3], protein-detergent complexes [4] and hollow microgel [5].

theory will be described and some recent applications to block copolymer micelles [3], protein-detergent complexes [4] and microgels [5] will be presented.

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14/11/2018

09:00 - 09:45

Novel DNA-Based Molecules and their Charge Transport Properties

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Charge transport through molecular structures is interesting both scientifically and technologically. To date, DNA is the only type of polymer that transports significant currents over distances of more than a few nanometers in individual molecules. Nevertheless and in spite of large efforts to elucidate the charge transport mechanism through DNA a satisfying characterization and mechanistic description has not been provided yet. For molecular electronics, DNA derivatives are by far more promising than native DNA due to their improved charge-transport properties.

In recent years we have invested great efforts to address the above issues. Measuring the charge transport in DNA was elusive due to great technical difficulties leading to carious results. We were recently able to devise an experiment in which double-stranded DNA is well positioned between metal electrodes. Electrical measurements give surprisingly high currents over 100 base-pairs (\sim 30 nm) elevated from the surface. The temperature dependence indicates backbone-related band-like transport.

In collaboration with the Kotlyar group, We were also able to synthesize and measure long (hundreds of nanometers) DNA-based derivatives that transport significant currents when deposited on hard substrates. Among the molecules metal containing DNA which is true metal-organic hybrid, a smooth and thin metal coated DNA and G-quadruplex DNA.

Step by step we improve the synthesized constructs and the measurement methods of single DNA-based molecules. I will present new and surprising results on dsDNA molecules. I will present new DNA-based molecules and report on our measurements of their properties.

- D. Porath, A. Bezryadin, S. de Vries, and C. Dekker, *Nature*, **403**, 635 (2000).
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09:45 - 10:30

Toward Electronically-Functional, Self-Assembling DNA Nanostructures

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Recent work has demonstrated that DNA, ordinarily considered a weak conductor, can be functionalized to carry electronic charge by site-specific incorporation of single silver ions inside the double helix via the non-canonical pairing of mismatched cytosines through Ag^+ coordination: (dC:Ag⁺:dC) [1, 2]. Through the alteration of sequence composition and cation availability, a variety of nanowires can be synthesized with tuneable length, ion distribution, and uniformity. These wires are more thermostable than Watson-Crick DNA, can shield intercalated Ag^+ from aqueous solvents, and are able to form in the absence of cluster contamination. We use computational sequence design algorithms to introduce nonlinear geometry to these nanowires, with the goal of creating self-assembling DNA nanostructures that may have potential for neural architectures from electrically-functional oligonucleotide components.

Linear Nanowires

The introduction of Ag^+ -coordinated sequence mismatches between opposing cytosine nucleobases does not significantly perturb the b-form helix of DNA [3]; and even in short, 11-mer polycytosines, this bond is able to withstand temperatures exceeding 90°C, avoid reduction by aqueous agents, and outcompete precipitants for Ag^+ . With careful buffer preparation, robust DNA nanowires can be produced for potential single-molecule electronic applications. Excess supply of Ag⁺ during annealing can affect the overall length of nanowires when sequences are designed to be promiscuous (e.g., through high cytosine density), while enzymatic end-end ligation can extend these wires up to ~100 nm in length. With a molecular conductance ~ $10^{-3}G_0$, this linear species is an attractive candidate for integration into devices or networks.

Branched Structures

Synthesis of DNA nanostructures that contain $dC:Ag^+:dC$ base pairs effectively changes the chemical language of assembly used to drive structure formation. As such, we have assayed a variety of nanostructures that require minimal-length oligomers in order to reduce the thermodynamic constraints that emerge from base pair promiscuity. We have explored several structures, including T-junction lattices based on the work of Hamada et al [4] (Figure 1), as well as Holliday junction and double crossover junction units based on foundational work from the Seeman group [5,6]. We explore the differences between rigid and flexible tiles using atomic force microscopy in both fluid and air, and suggest methods for the optimization of future structure design and assembly.

Computational Sequence Design

The addition of the dC:Ag⁺:dC base pair changes the lexicon of DNA assembly and drastically increases the likelihood of thermodynamic promiscuity among the nucleobases during structure formation. In order to drive accurate structure formation, we have developed a suite of software tools for the iterative optimization of DNA sequences with arbitrary pairing rules, editable geometry, and customizable local parameters. We designed a genetic algorithm to evolve solutions to this complex thermodynamic landscape *in silico* using a vectorized approach to heterostructure analysis. We present results based on this model, and we suggest a mathematical basis for dimer analysis for future applications.



Figure 1 Formation of a brick wall structure based on [4]. A) T-junction tiles are small units that bind using sticky ends and hairpin loops. B) This structure was imaged using high-resolution AFM and C) was shown to agree with the predicted lattice shape. D) Larger networks were observed, but the flexibility of the unit may preclude defect-free assembly at the micron scale.

Acknowledgements

We thank Ruojie Sha and Ned Seeman for help with design and synthesis. This work was funded by a National Space Technology Grant.

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10:50 - 11:35

Printing of Self-Assembled DNA Hybrid Materials

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The conductivity of DNA-templated nanowires is less than that of bulk material or other types of nanowire, and as their structure is granular they are not usually useful as interconnects. Single nanowire devices are ratherfragile and a single break can destroy the device completely meaning networks or bundles of nanowires are used instead. The simple drop-casting of DNAtemplated nanowires leads to the formation of networksdue to the intermolecular interactions as the liquid evaporates. However, this deposition process lacks control and the final pattern is of low resolution. On the other hand, inkjet printing is the controlled deposition of material at high resolution and has been routinely used to print conductive materials. Most conductive inks contain metal nanoparticles and are formulated at concentrations much higher than DNA-templated nanowires. Here we report the use of inkjet printing to prepare patterns of DNA-hybrid materials for electrical characterisation.

Cadmium sulfide can be templated onto λ -DNA molecules to form an aqueous dispersion of CdS/ λ -DNA nanowires. Subsequent addition of ethylene glycol to 50% v/v is sufficient to formulate an ink suitable for printing using piezoelectric drop-on-demand technology [1, 2]. Printed droplet arrays show a coffee-ring morphology of individual deposits by fluorescence and Raman microscopy, but upon increasing the number of layers of printed



Figure 1 Schematic showing the preparation of DNA-hybrid inks for ink-jet printing [1].

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Figure 2 Printed DNA hybrid tracks.

material by repeatedly printing over each droplet, the dry deposit approaches a disc shape. It is also possible to print parallel tracks, see Figure 2(a) and (b), by reducing the droplet separation in the array until neighbouring droplets overlap before they dry. The droplets coalesce to form a strip of width roughly equal to the diameter of the droplets.

The Marangoni effect drives the nanowires to the edges of the strip and when dry they form parallel tracks of CdS/ λ -DNA nanowire bundles. Both

droplets and tracks were printed onto Pt/glass interdigitated microelectrodes (10 μ m width, 10 μ m gap). The current-voltage characteristics of these two-terminal devices were approximately ohmic, but with some hysteresis, which was attributed to, coupled ion motion in the films.

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11:35 - 12:20

Synthesis of Long Double Stranded Concatemer Molecules by Self-Association of Short Single Stranded DNA Sequences

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In this work we reported synthesis of long (from hundreds to thousands base pairs) linear and circular double stranded (ds) concatemers composed of tandem oligonucleotide repeats. The concatemers were produced following a method published [1] almost 40 years ago from 5'-end phosphorylated half-complementary decameric or hexameric oligonucleotides (Figure 1, left panel) as well from the oligonucleotides containing modified nucleic bases or mismatched ones. Using the above method we synthesized various uniform linear DNA polymers, including telomeric DNA, as well as long (kbp) repeating single stranded DNA molecules. The advantage of the method is



Figure 1 A. - Schematic illustration of assembling of two single stranded decameric halfcomplementary oligonucleotides into a ds nucleic acid polymer. 1 – Hybridization of complementary fragments at 3'-ends of the oligonucleotides. 2 – Binding of the oligonucleotide dimers (step 1) to each other. Association of dimers with tetramers and structures composed of many oligonucleotide fragments being formed yields long concatemeric molecules. The oligonucleotides composing the polymer are covalently connected by DNA ligase (red arrows). Gel Electrophoresis (B, lane 2) and AFM imaging of DNA concatemers, assembled from a pair of half-complementary decameric 5'-end phosphorylated deoxyribonucleotides, ACGATGACGA and ATCGTTCGTC. he gel was stained with ethidium bromide. Lane 1 is a 1 kb DNA-ladder (the band corresponding to 1000 bp DNA is indicated by the white arrow). AFM was performed on molecules adsorbed on muscovite mica in a semicontact (tapping) mode.


Figure 2 A. - Schematic drawing of ds concatemers prepared as illustrated in Figure 1A from decameric oligonucleotides containing mismatches (A), 5-methilcytosine nucleotides (B) and a Fluorescein-modified nucleotides.

that it enables incorporation of artificial nucleotides along the whole length of the DNA. We have synthesized long (hundreds of nanometers) concatemeric dsDNA molecules containing: methylated cytosine nucleotides, fluorescent dyes-labeled nucleotides and mismatched base pairs (Figure 2). The modified nucleotides can be introduced into one or both strands composing the double helical polymer. The frequency of occurrence of the modified nucleotides in the DNA can be varied. We have prepared concatemers comprising a mismatched pair of bases per every 5 or 10 base pairs in the sequence. The latter molecules cannot be synthesized either by chemical methods (due to the length limitation) or by DNA polymerase. The DNA molecules comprising reactive groups capable for anchoring metal particles or/and other redox active elements along the nucleic acid polymer can be used as wires or transistors in future nanoelectronic devices and circuits.

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13:00 - 13:45

Single Molecule Fluorescence Investigations of DNA-based Self-Assembled Structures

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DNA can fold into a number of secondary structures that play a role in the regulation of gene expression [1]. It can also be harnessed as a building block in the field of DNA nanotechnology to create both static and dynamic DNA structures of all shapes with sizes ranging from a few to several hundreds



Figure 1 A) and B) CCD images of surface-immobilized DNA G-quadruplex structures labelled with two different fluorophores, each imaged in its color channel shown in green and red, respectively. Each spot shows fluorescence from individual DNA molecules. C) Förster resonance energy transfer (FRET) efficiency between the two fluorophores as a function of time. The time trace shows conformational changes of a single DNA molecule.

of nanometers [2]. Owing to their phenomenal addressability, these DNA nanostructures are attractive platforms for organizing matter at the molecular level and provide high flexibility for positioning fluorescent molecules.

To obtain insights into structural dynamics of natural and artificial DNA structures, we used single molecule fluorescence microscopy. The method allows resolving the different conformations of these structurally heterogeneous systems and studying the properties of fluorescent molecules arranged onto DNA templates. I will present our single molecule fluorescence data analysis platform [3] and investigations of the structural heterogeneity and dynamics of different DNA structures [4, 5] and of fluorescent DNA modified conjugated polymers [6, 7]. Our results give insights into DNA folding and local structure as well as guidelines to achieve nanoscale spatial control of fluorescent molecules.

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13:45 - 14:30

Probing the Dielectric Constant at the Nanoscale: From Thin Films to DNA and Confined Water

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The dielectric constant (or electric polarizability), ϵ_r , is a fundamental physical property of matter which depends on chemical composition, structure and phase. It plays a crucial role in a wide range of phenomena and disciplines, from physics and materials science to chemistry and molecular biology. For example, in physics, it is inherently linked to charge storage and electric transport. In biology, it modulates long-range electrostatic and van der Waals interactions that are crucial for macromolecular assembly and interactions. Yet, probing local dielectric properties has remained a long-standing technical challenge because the signals that have to be detected are extremely weak and buried into non-local and geometric artefacts.

In the first part of my talk, I will review our work in which we showed that the dielectric constants of nanostructures and biological molecules can be measured at low frequencies (<1 MHz) with a scanning probe using both the current-sensing [1, 2] and electrostatic force-sensing [3, 4] approach. We determined the dielectric constants of a variety of nanostructures and biological samples for the first time: from thin oxides and biological membranes [1, 2, 6] to single nanoparticles [3], viruses [3, 4] and bacteria [5]. Importantly, we resolved the dielectric constant of DNA in a native condensed state [4], which had remained unknown. We found it \sim 8, sensibly higher than commonly assumed in theoretical calculations, and showed that it is a critical parameter for a realistic computational description of DNA-DNA and DNA-protein interactions. Furthermore, we showed that local dielectric measurements can be done in electrolytic environment [7], which is of great importance for electrochemical and biological applications, and extended up to the microwave regime (GHz frequencies) [8].

In the second part of my talk, I will present our latest results in which we were able to measure the dielectric constant of few water layers confined between two atomically thin crystals [9]. For many decades, it has been

speculated that the dielectric constant of water near surfaces should be different from that of bulk water. This has major implications because water's dielectric constant directly affects various forces between microobjects and macromolecules. In turn, these forces define many fundamental phenomena in nature such as hydration, ion solvation, chemical reactions and macromolecular assembly, to name but a few. Despite a massive amount of literature and of atomistic simulations, the absolute value of the dielectric constant of near-surface water and how far its anomalous behavior (if any) extends into the bulk had remained unclear so far. Our experiments revealed the presence of an interfacial layer with vanishingly small polarization such that its out-of-plane ϵ_r is only ~2. The electrically dead layer is found to be two to three molecules thick, in agreement with the thickness predicted by molecular dynamics calculations. Our results provide much needed feedback for theories describing water-mediated surface interactions and behaviour of interfacial water, and show a way to investigate the dielectric properties of other fluids and solids under extreme confinement.

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14:30 - 14:50

Fabrication of DNA Concatemers Containing Multiple Modifications

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Here we describe the construction of double stranded (ds) concatemers composed of short (6–10 bases) repeating tandem oligonucleotides units containing modified nucleotides. The synthesis of incudes: self-association of the 5'-end phosphorylated half-complementary oligonucleotides into long (hundreds of base pairs) ds nucleic acid polymers and covalent linkage of the oligonucleotides in the strand by DNA ligase (Figure 1B). The oligonucleotides containing various modified nucleotides can be assembled into long (hundreds of nanometers) ds concatamers. One of these nucleotides is amino-modified thymine in which the amino group is linked to 5-position of the pyrimidine ring via two or six carbon atom spacer arms. The amine group can be conjugated to amine reactive derivatives of various organic dyes and nanostructures. However, since the presence of modified bases should affect the base stacking in DNA in this research we have been mostly focused on attached of functional groups to the nucleic acid's backbone. This was done through conjugation of the iodoacetamide derivatives of molecules of interest with a phosphothioate group (groups) of one of the half-complementary nucleotides (see Figure 1A). We have conjugated the iodoacetamide derivative of fluorescein (5-iodacetamido-fluorescein) to the phosphorothioate residue of the decameric oligonucleotide as shown in Figure 1A. The modified oligonucleotide was separated from the excess of the dye and purified to homogeneity using size-exclusion chromatography and ion-exchange HPLC. The purified oligonucleotide was incubated with an equimolar concentration of the half-complementary one in the presence of DNA ligase (see Figure 1B). The synthesized molecules were purified by HPLC and analyzed by electrophoresis (see Figure 1C). The resulting DNA molecules (about 250 bp) were highly fluorescent and can be visualized on the gel without staining with Ethidium Bromide (Figure 1C, left panel). By varying experimental conditions one can produced longer or shorter

Fluorescein-labeled concatemeric molecules. We have also synthesized concatemers labeled with another fluorescent dye, 5-naphthalene-1-sulfonic acid (IAEDANS) and molecules containing both the above dyes.

The concatemers containing reactive groups along the whole length of the polymer can be used as templates for synthesis and assembly of novel materials and nanostructures.



Figure 1 A) - Schematic illustration of conjugation of a phosphorothioate residue with 5-iodacetamido-fluorescein (IAF). The dye interacts specifically with phosphorothioate residues; native nucleotides cannot bind IAF. B) – The decameric oligonucleotide containing one phosphorothioated residue is being labeled with IAF (reaction 1). The labeled oligonucleotide forms a dimer with the half-complementary not-labeled one (reaction 2). The oligonucleotide dimers formed are being associated into long ds nucleic acid polymers in the presence of DNA ligase. The enzyme covalently links the gaps between the tandem oligonucleotide blocks in the strands (red arrows). C) - Gel Electrophoresis of the synthesized Flu-labeled DNA concatemers (see B) Ohe gel was illuminated by a blue light illuminator (at 470 nm); the image was taken by a digital camera (left panel) or stained with ethidium bromide and imaged on a common gel imaging system (right panel). Lane 1 is a 1 kb DNA-ladder (the band corresponding to 250 bp is indicated by the white arrow).

15:10 - 15:55

Self-Assembly of Block-Copolymer Structures for In-Situ Nano-Lithography

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In this paper we report how block-copolymer (BCP) self-assembly of polystyrene–b–polydimethylsiloxane (PS–PDMS) is used for in-situ nanolithography to fabricate hexagonally ordered nanostructures on the surface of Si[1]. This is done by forming an in-situ etch mask on the Si surface by spin coating of the BCP in solution and subsequent solvent annealing, and reactive ion-etching (RIE) steps. The wetting properties of the fabricated structures are studied to reveal a multitude of possible wetting and anti-wetting configurations, depending on the subsequent fabrication and surface coating steps[2].



Figure 1 a) In-situ etch mask fabricated SF_6/O_2 RIE after solvent annealing of a thin PS-PDMS block-copolymer spin-coated film on a polished Si wafer surface. b) Pattern transferred by Cl_2 RIE into Si. Scale bar is 200 nm in both panels.

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15:55 - 16:15

Molecularly Guided Assembly of Colloidal Nanoparticles in Solution and on Substrates

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Plasmonic nanoparticles are increasingly important tools in sensing, drug delivery and catalysis, but an increasing number of synthetic and assembly techniques are required to design the desired nanostructures. Synthesis of nanoparticles and the assembly of these particles into larger combinations typically fall into two categories: top-down methods, typically using lithographic or nanoimprinting techniques, and bottom-up synthesis, typically using molecularly guided self-assembly of colloidal particles. There are advantages for each method, primarily associated with the control of assembly in the top-down methods versus the versatility and variety of colloidal particles available for the bottom-up synthesis.

In this presentation, we review two applications of molecularly guided assembly of nanoparticles. The first application utilizes an entirely colloidal self-assembly method to systematically combine gold nanoparticles into dimers with very short separations [1]. The separation range can be controlled through varying the concentrations of the molecular linker, DNA, on the surface of the particles. Additionally, changing the DNA concentration reveals that at separations below 3 nm, the charge transfer through the DNA molecules in the gap reduces the plasmon coupling. This results in a decrease



Figure 1 A) DNA-directed self-assembly of nanoparticle dimers with different concentrations of linker molecule. B) Sample spectrum (blue), simulated spectrum (red) and expected wavelength (black dashed line) of imaged nanoparticle dimer. Scale bar = 5 nm.

in the observed plasmon shift as well as a decrease in the electric field enhancement. Further reduction in the observed plasmon shift occurs when the charge transfer capabilities of DNA linker are enhanced through the DNAdirected deposition of small palladium nanocrystals in the gap, which allows for more charge movement through the gap [2]. This increases the observed depolarizing of the plasmon coupling to a separation of over 4 nm.



Figure 2 A) Schematic of gold nanodisks with palladium nanocubes absorbing hydrogen. B) Palladium nanocubes binding to gold nanodisks. Scale bar = 100 nm.

The second application of molecularly guided assembly demonstrates the use of molecular components to create an electrostatic differential on lithographically patterned surfaces in order to attract colloidal nanoparticles with an opposite surface charge. This technique has been utilized to attach negatively charged palladium nanocubes to patterned gold nanodisks that are modified with molecular components to create a positive surface charge. The palladium nanocubes are subsequently used as a hydrogen sensor, where the gold plasmon resonance serves as a monitor for the change in the permittivity and volume expansion of the palladium as is absorbs hydrogen [3]. Additional uses for the molecular assembly on lithographically designed substrate are being explored in nanofluidics, other sensing applications and catalytic routes.

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16:15 - 17:00

Self-recovery, Fatigue and Anti-fatigue of Supramolecular Elastomers

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Supramolecular elastomers (SMEs) are three-dimensional networks of polymer chains bridged by covalent cross-links and non-covalent bonds with finite lifetimes. The reversible non-covalent bonding is based on (i) metalligand coordination, (ii) electrostatic interaction, (iii) hydrophobic association, (iv) hydrogen bonding, and (v) host-guest recognition. An advantage of these materials compared with conventional vulcanized rubbers and thermoplastic elastomers is their ability of rapid self-healing after damage at ambient temperature. The mechanical response of SMEs is characterized by (i) rapid relaxation of stresses (with the characteristic time of a few minutes), (ii) self-recovery (a monotonic reduction in plastic strain with time after cyclic loading), and (iii) anti-fatigue (an increase in maximum stress with number of cycles under deformation programs with intervals of recovery between cycles).



Figure 1 Self-recovery of PB-TAA elastomer. Symbols: experimental data. Solid lines: results of simulation.

A constitutive model is developed for the viscoelastic and viscoplastic behavior of supramolecular elastomers. Stress-strain relations are derived from the free energy imbalance inequality for an arbitrary three-dimensional deformation with finite strains. The viscoelastic response reflects breakage

and reformation of temporary bonds in a transient polymer network (transition of chains from their active to dangling state and vice versa). The viscoplastic response reflects slippage of permanent junctions with respect to their reference positions. The model is applied to fit experimental data in tensile loading-unloading tests, relaxation tests, and multi-cycle tests on several SMEs. Numerical simulation shows that the governing equations describe adequately the experimental stress-strain diagrams, the material parameters evolve consistently with chemical composition of SMEs and experimental conditions, and predictions of the model are in agreement with observations.

Financial support by the Danish Innovation Fund (project 5152-00002B) is gratefully acknowledged.

15/11/2018

09:00 - 09:45

The Last Nanometer – Hydration Structure of DNA and Solid Surfaces Probed by Ultra High Resolution AFM

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Recent advancements in atomic force microscopy facilitate atomic-resolution three-dimensional mapping of hydration layers next to macromolecules and solid surfaces. These maps provide unprecedented information on the way water molecules organize and bind these objects. Since the hydration structure governs the energetics of solvation and interactions between objects immersed in solution, the new data are invaluable when trying to resolve fundamental questions such as identification of molecular binding sites and interaction mechanisms.



Figure 1 (a) An ultra high resolution image of DNA with a reference model of B-DNA. The major grooves, minor grooves and top-facing phosphates are highlighted with gray and white arrows on the model and the scan. Scale bar, 5nm. (b) Hydration of double stranded DNA. Red shaded pixels mark the position of labile water molecules.

After a short presentation of our home-built microscope, characterized by sub 0.1Å noise level, the talk will focus on two representative studies. The first one will disclose our recent finding [1] that in solutions in contact with atmosphere, hydrophobic surfaces are generically coated with a dense layer of adsorbed gas molecules. This layer renders the hydrophobic interaction a certain universality, regardless of the underlying surface. The second study will present our recent success [2] in obtaining ultra high resolution images of DNA and 3d maps of its hydration structure (e.g., Figure 1 below). This study shows that labile water molecules concentrate along the DNA grooves, in agreement with known position of DNA binding sites.

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09:45 - 10:30

Frictional Behavior of Two-Dimensional Materials

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Friction occurs when surfaces of solid bodies touch and move against each other. Energy is thereby converted into heat that is lost. In order to reduce the friction in the metallic elements during sliding, for example in automobiles or industrial machines, materials with a lamellar structure are commonly used as the solid lubricants. One of the dry lubricants is graphite, which has a three-dimensional layered structure.

Graphene, a two-dimensional carbon sheet, has received much attention in the past few years due to its unique mechanical, electronic properties. Earlier work has shown that the frictional behavior of graphene exhibits traits unlike those of conventional bulk materials. It has been shown experimentally that monolayer graphene shows higher friction than multilayer graphene and graphite [1]. When an atomic force microscope (AFM) tip slides on few-layer graphene loosely adhering to a substrate, the static friction force gradually strengthens for a few initial atomic periods before reaching a constant value. Such transient behavior, and the associated enhancement of steady-state friction, diminishes as the number of two-dimensional layer increases. Although a wide range of suggestions have been proposed [1, 2], the mechanism behind this remains subject to debate.

Using atomistic simulations, we reproduced the experimental observations of layer dependent friction and transient frictional strengthening on graphene [3]. Atomic force analysis reveals that the evolution of static friction of graphene is strongly related to the re-adjustment of its configurations as a direct consequence of its greater flexibility. Upon sliding the tip atoms



Figure 1 Frictional behavior for a Si tip sliding over a graphene/a-Si substrate system.(a) Model setup in atomistic simulations. The black, red and gold atoms refer to the a-Si substrate, graphene and the tip, respectively. (b) Illustration of distribution of atomic friction force at tip/graphene interface. (c) Friction force trace in multilayer graphene.

become more strongly pinned and show greater synchrony in their stickslip motion. While the quantity of atomic-scale contacts (true contact area) evolves, the quality (in this case, the local pinning state of individual atoms and the overall commensurability) also evolves in frictional sliding on graphene.

The current findings are critical for explaining the time-dependent friction of configurationally floppy interfaces. It also suggests a means of controlling friction of two-dimensional materials via strain engineering.

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10:50 - 11:10

Study of Two Dimensional Electron Gas Formation at AlGaN/GaN Interfaces using Kelvin Probe Force Microscopy

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AlGaN/GaN heterostructures are of high research and industrial interest for the production of high electron mobility transistors utilizing the twodimensional electron gas (2DEG) induced at the interface due to polarization effects. Critical AlGaN thickness is an important practical parameter which is under the study in this work.

Ultrathin layers of AlGaN (between 2–12 nm thick) are grown on top of GaN in order to study 2DEG formation. The structures are prepared using the metal organic chemical vapour deposition method. Combining Rutherford backscattering, X-ray photoelectron spectroscopy and ion sputtering the composition and thickness of the AlGaN layers are found. The measured thicknesses agree well with the expected values. For selected samples, TEM analysis is also performed showing quality of the interfaces. Al/Ga ratio is found to be nearly constant, 0.26–0.28, in layers thicker than 5–6 nm. In the thinner films, estimation of the composition is unreliable due to the photoelectrons coming from the underlying GaN film. Kelvin probe force microscopy (KPFM) is used to study surface potential depending on AlGaN layer thickness.



Figure 1 KPFM images of (a) GaN, (b) AlGaN(3.5 nm)/GaN and (c) AlGaN(12 nm)/GaN.

Pure GaN samples show homogeneous potential distribution across the surface (see Figure 1a) with a mean value of 0.72 ± 0.3 V. This corresponds to an upward band bending of 1.1 ± 0.1 V. Both values are in good agreement with previous measurements [1]. Overall, the contact potential difference rises from pure GaN to AlGaN/GaN following the theoretical estimates for these compound semiconductors. Growth of thin (ca. 2 and 4 nm) layers of AlGaN leads to a mosaic-like potential distribution indicating that 2DEG is formed at the interface but it is not continuous because of the low layer thickness and poor stoichiometry (see Figure 1b). Homogeneity of the surface potential maps increases for layers thicker than 7-8 nm (Figure 1c) allowing to conclude about critical thickness of AlGaN for the formation of continuous 2DEG. Similar findings on critical thickness of a barrier layer for the formation of 2DEG were reported using KPFM for LaAlO₃/SrTiO₃ heteroiterfaces [2]. The obtained results are also in good correlation with earlier data reporting 2DEG observations for AlGaN layers thicker than 3.5 nm in which the mobility and charge carrier concentration increase reaching maximal values for the layers at around 10 nm [3, 4]. Thus, the work brings important insights into registration of 2DEG at AlGaN/GaN interfaces using KPFM.

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11:10 - 11:55

Probing Local Electronic Property of Two-dimensional Materials by Atomic Force Microscopy

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Compared to zero-bandgap graphene, 2D layered transition metal dichalcogenides (TMDs) with the chemical formula MX_2 (where M–group IVB–VIIB metal and X–chalcogen) have brought new possibility for the applications in ultralow-power electronics due to the reasonable bandgap. Currently, the carrier mobilities of TMDs at ambient conditions are a little bit low which limit their practical applications. Many strategies, for example synthesizing new member of 2D TMDs, revealing the transport mechanism and optimizing the device configuration are acknowledged as the promising methods. Except metallic and insulate property, many 2D layered materials exhibit semiconducting behavior including n-type, p-type or ambipolar, which could be used to fabricate various electronics. Compared to unipolar (n-type or p-type) transistors, ambipolar transistors, which can easily switch between n-type and p-type behavior by applying an electric field, are most promising candidates since they can effectively simplify circuit design and save the layout area in CMOS.

In this presentation, scanning probe technique including electric field microscopy, kelvin probe force microscopy and current atomic force microscopy, will be introduced to study the local electronic property of 2D layered semiconductor. The surface potential, aligned energy band in p-n junctions and local carrier transport property of CVD-grown PtSe₂ will be talked [3–5]. Furthermore, the dimensionality dependent ambipolar WSe₂ will be introduced from locally field screening and tuned work function under external electric field.

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12:40 - 13:25

Sense and Sensitivity: SERS-based Assessment of Mitochondrial Bioenergetics

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Selective and sensitive investigation of components of the electron transport chain in functional mitochondria is important for fundamental biophysical research and for development of new biomedical diagnostic tools. Up-to-day methods – fluorescent microscopy, absorption spectroscopy and registration of oxygen consumption – provide only indirect information about the redox state of electron transport chain complexes. We suggested a novel label-free approach based on the surface-enhanced Raman spectroscopy (SERS) to monitor conformational changes and redox state of cytochrome c in electron transport chain of functional mitochondria [1]. We demonstrated that hierarchical silver nanostructures ensure intensive enhancement of Raman scattering of cytochrome c in mitochondria without affecting their morphology and respiration [2]. Our studies revealed:

- High *sensitivity* of SERS spectra of cytochrome *c* in mitochondria to the activity of complexes of electron transport chain, to the rate of ATP synthesis, to mitochondrial membrane potential, and to mitochondria morphology;
- High *selectivity* of different wavelength laser excitation to access certain alterations: (i) redox transitions in cytochrome c (488 nm); (ii) conformational and motility changes in heme of cytochrome c (514 and

532 nm), (iii) redox and conformational properties of cytochromes a/a3 (633 nm), and (iv) state of outer mitochondrial membrane (785 nm);

• High *detectability* of pathological changes; SERS methodology allowed to trace the differences in cytochrome *c* of functional heart mitochondria in control and spontaneously hypertensive rats. This opens new perspectives for development of SERS-based tools to follow the progression of cardiovascular diseases.

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13:25 - 14:10

Gold Nanostar Assays for Oncology and Virology

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Plasmonic nanostructures are well-known as effective substrates for applications in which near field enhancements are sought. In particular, we have shown that gold nanoparticles can be employed to carry out identification of U87 glioblastoma cells with surface enhanced Raman spectroscopy (SERS), by targeting overexpressed $\alpha V\beta$ 3 integrins via RGD peptides [1]. However, gold nanostars have been shown to lead to much higher field enhancements, owing to their uniquely sharp protruding spikes. In particular, we have shown how they can be employed to build sensing platforms for the direct identification of small molecule analytes by SERS achieving femtomolar limits of detection [2]. We have also demonstrated how gold nanostars can be tethered to rigid substrates and conjugated in situ to aptamers for targeting and recognition of prostate cancer cells and enable the quantification of cancer cell biomarkers at the single cell level [3]. In this talk I will also present how SERS-based quantification of prostate specific membrane antigen (PSMA), a promising biomarker for prostate cancer diagnosis, enables discrete patient stratification, and how gold nanostars can be uniquely employed for the identification of influenza virus mutations at the single cell level with no interference from protein corona.



Figure 1 Gold nanostar substrates functionalized with EpCAM-specific aptamers enable to achieve 50% yield in cell capture and quantification of the biomarker at the single cell level.

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14:10 - 14:30

Optical Resonances and Field-enhancement in 3D Metal Nanorods

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In this paper the optics of single and coupled 3D metal nanorods in solution is considered theoretically using the Electric-Field Integral Equation (EFIE) [1]. The extinction, scattering, and absorption cross section spectra, and field enhancement distributions, will be presented at the conference for a range of single rod geometries, and for configurations of rods with e.g. varying lengths and separation.

An example of the extinction cross section spectra for single rods with a radius of 5 nm and different lengths h is shown in Figure 1(a). Here, the rods are illuminated with a plane wave polarized along the z-axis (along the rods) and propagating along the x-axis. The resonance seen in the spectra clearly redshifts with the rod-length h, and it is thus possible to control the resonance via the geometry. An example of the enhancement of the magnitude of the electric field is shown in Figure 1(b) for rods with the length h = 30 nm at the resonance wavelength.



Figure 1 (a) Extinction cross section spectra of gold nanorods in water with radius 5 nm and different lengths h. (b) Enhancement of the electric-field magnitude at resonance for h = 30 nm. The rods are illuminated with light polarized along the rod axis (z).

At the conference similar calculations will also be presented for other rod geometries with e.g. flat ends instead of rounded ends and for configurations of two rods separated by a small or large gap. In the latter case the resonance wavelength will be shown to be highly sensitive to the gap size, and more so for rods with flattened ends. The field enhancement is on the other hand higher for rods with rounded ends. With two rods, each being similar to the one considered in Figure 1(b), and with a 1–nm gap, the field enhancement at resonance is app. 400.

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14:50 - 15:35

Large-Area Molecular Electronic Devices from Self-Assembled Monolayers

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A central goal in molecular electronics is to understand charge transport properties of single molecules and their ensembles. This fundamental knowledge may ultimately pave the way for electronic components constructed from tailor-made molecular building-blocks that can overcome some limits of conventional silicon-based microelectronics. The formation of robust and reproducible contact between molecule and electrode is a key challenge. At the single-molecule level, we have recently explored the use of parallel self-assembly strategies towards the formation of multiple single-molecule junctions, wherein the molecule-electrode interface is controlled with atomic precision [1]. However, the use of self-assembled monolayers (SAMs) offer a complementary approach for fabricating molecular electronic devices that are more amenable to device integration and up-scaling [2].

The presentation will highlight recent progress from our group on the fabrication and characterization of large-area molecular electronic devices employing chemically derived graphene as a soft contact-interface to the molecules. The graphene material serves a dual purpose in that it protects the underlying monolayer from filamentary damage when evaporating a metal top electrode, while itself functioning as a transparent, conducting electrode. The resulting solid-state devices are robust, permanent and can accommodate a diverse range of functional molecular layers, including e.g. photo-, redox- and bias-switches [2, 3], as well as a range of molecular binding groups. Further advancement in the chemical fabrication and processing of the graphene material has recently enabled reliable measurements of our devices at cryogenic temperatures and facilitated the measurement of inelastic electron tunneling spectroscopy (IETS) [4, 5].



Figure 1 Schematic illustration of solid-state large-area molecular electronic device platform using a graphene material as a soft top-electrode for contacting the underlying molecular monolayer.

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15:35 - 16:20

Kinetics of a Solid-Solid Charge Transfer Reaction

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We present a detailed analysis of the kinetics of electron transfer at a solidsolid interface. The study was enabled by measuring the conductance of ultra-thin (< 50 nm), fully suspended single-crystalline silicon nanowires with several well-defined surface chemistries [1]. The measurement had a dynamic range across 7 orders of magnitude with a detection sensitivity of order single event over a $10^3 \ \mu m^2$ reaction area. We find that classic, firstorder process [2, 3] is unable to capture the reaction progress and propose a new kinetic model based on a continuum of reactant geometries inherently present at typical solid-solid interfaces. The new model captures the kinetic manifestation of heterogeneity in a single, global rate constant. Quantitative agreement with data and an analysis of the parameters suggest that this model may be generally applicable to charge transfer at solid-solid interfaces.



Figure 1 Illustration of a nanoscale charge transfer reaction interface. Cobaltocene molecules (orange) on top of a 3-carbon monolayer covalently attached to atomically-rough Si(100) (purple). One positively-charged cobaltocenium ions (crimson sphere) transferred an electron (green) to the lattice. A Si(111) microfacet is depicted with a silicon-fluorine (cyan) defect. Such surface defects result from the fabrication of nanoscale materials and devices.

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16:20 - 17:05

Luminescence Spectroscopy of Rhodamine Homodimer Dications *in Vacuo*

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The photophysics of dyes strongly depends on their microenvironment, either solvent molecules or nearby charges. Also interactions with other dyes affect the spectroscopical properties. For ionic dyes it can be difficult to quantify the interactions due to solvent screening and/or nearby counter ions. To shed light on intrinsic properties, it is advantageous to perform luminescence experiments in the gas phase, which, however, requires specialized apparatus. In Aarhus we have constructed the LUNA setup, LUminescence iNstrument in Aarhus (Figure 1) [1] that allows us to measure fluorescence from larger ions produced by electrospray ionization. We used this setup to study rhodamine monomer cations as well as homodimers where the two dye cations are separated by methylene linkers, $(CH2)_n$. I will present the results and compare to spectra measured in solution. Indeed, in the gas phase, we measure significant redshifted emission when there is a nearby charge while in solution solvent screening reduces this effect to almost nothing. The impact of nearby charges may have implications for gas-phase Förster Resonance Energy Transfer experiments where the aim is to reveal the structures of biomolecular ions in the gas phase.



Figure 1 LUNA for gas-phase luminescence experiments on molecular ions.

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16/11/2018

09:00 - 09:45

Preparation of Protein Materials for Applications in Photonics and Bioelectronics

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Natural materials often display hierarchical organization of nano-structures, lending unique properties to the macroscopic material. Many proteins are able to self-assemble into ordered nano/micro-structures, and it is interesting to investigate applications of such structures in materials science. However, for many applications it is desirable to have additional functionality, not present in the original protein. It is therefore desirable to develop methodology for functionalization of protein materials. We have developed novel techniques for preparation of functionalized protein 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 selfassembly into functionalized fibrils. The process can be performed simply with mortar and pestle [1-3] or with automated milling equipment [4]. These fibrils can then be induced to undergo colloidal assembly into materials. In this presentation will be given examples of such materials preparation, and applications of the materials in photonics and bioelectronics will be presented.

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09:45 - 10:30

Molecular Dynamics Simulations of CRISPR/Cas9

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Class 2 CRISPR (clustered regularly interspaced short palindromic repeats) systems offer a unique protocol for genome editing in eukaryotic cells and has already been validated in many organisms [1]. In genome editing through CRISPR, the target DNA is first recognized by a complementary RNA bound to an endonuclease. The RNA-guided DNA unwinding leads to formation of a RNA-DNA hybrid duplex and a displaced DNA strand (Figure 1). Thereafter, the nuclease portion of the Cas9 protein closest to the DNA cleavage site attains a conformation essential for concerted DNA cutting.

The nuclease activity of Cas9 can be also get triggered when there is imperfect complementarity between the RNA guide sequence and an off-target genomic site, which is a major limitation of the CRISPR technique [2] for therapeutic applications. Our goal is to understand the binding mechanisms in CRISPR/Cas9 for predicting ways to increase its specificity.



Figure 1 Representation of the crystal structure of a ternary CRISPR/Cas9 complex (PDB ID 4UN3). The cyan and black DNA strands represent the target and non-target DNA strands respectively. The target DNA strand is involved in RNA-DNA hybrid formation with a 20 base long segment of RNA (orange). The protein is represented with surfaces.

We have performed classical MD simulations of CRISPR/Cas9 ternary complexes with the wild type Cas9 [4] and three mutations: K855A, H982A and the combination K855A+H982A, selected from the results of experimental work [3]. Our initial results reveal significant structural impact of the mutations. We find that the unwound part of non-target DNA strand shows highest structural changes for the combination mutation. The distance between the HNH domain of Cas9 and the unwound non-target DNA strand is significantly affected by different mutations, with possible implications for specificity.

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10:50 - 11:35

Colloidal Lithography Approaches to Study Plasmon Coupling and Plasmonic Devices

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In the last two decades a wide range of nanofabrication approaches have been developed based on top down lithography or bottom up self assembly. Here approaches based on colloidal monolayer masks combined with cleanroom processing such as Sparse Colloidal Lithography (SCL) [1] and Hole Mask Colloidal Lithography (HMCL) [2] will be presented. Traditionally these approaches have given arrays of circularly symmetric structures such as disks [3], holes [4], rings [5] and cones [2]. More recent approaches have allowed post-modification of the masks to change their size [6] or their shape. Colloidal lithography approaches have proven appropriate to allow arrays of novel plasmonic structures to be fabricated to study plasmon coupling [7], refractive index sensitivity [8] and chiral properties of arrays [9]. In this paper we report on a number of new fabrication approaches based on programmable angled evaporation, or post or pre-modification of colloidal masks. Figure 1 shows a range of post-modifications that can be made to the masks materials in HMCL and SCL to generate new structures. Specific examples of sensational biosensing [10] chiroptical materials and novel structures will be made. In situ deposition of sacrificial material of dielectric (e.g. Silicon oxide or Aluminium oxide) or metal (e.g. Silver or Aluminium) can be used to prepare mask materials that can be modified within the process and generate a systematically varied set of samples. Examples will be given of subtractive processes to generate 2D and 3D structures by first depositing silicon oxide or aluminium which is later removed by etching to generate asymmetric plasmonic structures. Other examples will be given of processes depositing silicon oxide mask materials registered to the colloidal nanoparticle defined patterns to allow fabrication of rings, crescents and asymmetric rings. Examples of final structures will be given.



Figure 1 Schematic representation of mask modifications in Hole Mask Colloidal Lithography (HMCL) and Sparse Colloidal Lithography (SCL).

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Effects of Remote Substituents on Electrochemical Reduction of X-PhCH=NPhCH=CHPh-Y

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Schiff-bases have prospective applications in functional technologies such as organic photovoltaic [1] and other molecular electronic devices [2]. Therefore, for the design of molecular optoelectronic devices of high efficiency, it is hence of great interest and significance to understand the relationship between structure and electrochemical property of Schiff bases in the molecular level [3]. However, Schiff base displays a high degree of complexity that makes it difficult and expensive to elaborate this in a large scale. Consequently, quantitative structure-property relationship (QSPR) focusing on simple, cost-effective and easily scalable Schiff bases has emerged [4].

In this paper substituent effects on the electrochemical properties of X-PhCH=NPhCH=CHPh-Ycompounds with long conjugated backbone were studied from the viewpoint of reduction potentials ($E_{(red)}$). The reduction potentials of 28 compounds of this kind were determined by cyclic voltammetry, and the effects of X and Y as substituents on ($E_{(red)}$) were explored separately by experimental and computational methods, and their contribution on $E_{(red)}$ was investigated. The results show that the introduction of a styryl group promotes conjugation, leading to a shift of $E_{(red)}$ in the positive direction. Electronic effects, especially resonance effects of substituents, play



Figure 1 Radical anion of XBAY and XBASBY and their energies relative to CNBASBCN, whose energy level is defined as zero.

a key role in tuning the ($E_{(red)}$) of XBASBY. Also, with the increase of conjugated chain length, $E_{(red)}$ becomes more dependent on the effects of the excited states of X and Y. A quantitative model is developed to express the effects of remote substituents on $E_{(red)}$, which is confirmed to be reliable by lee-one-out method. In particular, the remote substituents Y cause effects on $E_{(red)}$ enhancement rather than attenuation. The experimental results can be clarified based on the calculation results of frontier molecular orbital and band gap energies. Also, the relative energies of radical anion were proposed by DFT method to explain the role of the styryl group (Figure 1).

Given the effects of styryl group and substituents, it is anticipated that the $E_{(red)}$ of Schiff bases can be adjusted by controlling the distance between substituents and -CH=N- center. It is envisaged that by extending the molecular conjugated length, the electrochemical properties of Schiff-base compounds can be effectively tuned for applications in areas of organic photovoltaic-like molecular electronic devices.

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Screening for Functional Peptide Based SsGPRC6A to Recognize L-amino Acids Specifically by Molecular Docking and Dynamics Simulation

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One of the most important function of G protein-coupled receptors family C subtype 6A (GPRC6A) recognizes and responds to L-amino acids as its principal physiological ligand. In this study, homology modeling, molecular docking and molecular dynamics simulation were performed to explore structural features and binding mechanism of L-amino acids on SsGPRC6A of Sus scrofa, and to construct model containing the binding domain of the ligands for searching functional and special polypeptide to recognize the L-amino acids respectively. The homology model of SsGPRC6A was constructed using the crystal structure of the extracellular region of the group II metabotropic glutamate receptor (2E4U) at 2.35 Å resolution as template. The homological models for SsGPRC6A were constructed by the method of Swiss model and EasyModeller4.0. The constructed models were evaluated and docked by using the online servers and Discovery studio 2.5. Twenty L-amino acids were docked in the active site of the obtained model by autodock program. The results indicating the quality of all the models generated by Swiss model is higher than that of the models generated by EasyModeller4.0 by 45.1%, the model is better than that of the models were minimized of free energy. After docking, the constructed model and the favorite ligands complex were put into a TIP3P water box, a 20 ns molecular dynamics (MD) simulation was performed on the whole system. The model with a high-affinity binding site in active pocket interact with broad-spectrum amino acids by hydrogen bond as well as hydrophobic interaction. And the model have binding preference and stability for basic and aromatic amino acids. Thus, the findings from this study will be helpful for predicting and elucidating the binding pattern of SsGPRC6A to L-amnio acids.

The study was supported by the National Natural Science Foundation of China (81874332), the China Scholarship Council (CSC201708430265, CSC201708430266 and CSC201708430267), the Natural Science Foundation of Hunan Province (2017JJ3048, 2016JJ2037), and the Postdoctoral Science Foundation of China (2017T100601, 2016M590746).

Immobilization of Recombinant β -Glucosidase on Magnetic Nanoparticles and its Potential in Production of Ginsenoside F_2 and Compound K

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In the present study, *BbBgl* gene was cloned and expressed in *E. coli* BL21. The β -glucosidase was purified by Ni-NTA magnetic beads to obtain an enzyme with specific activity of 37 U/mg protein using pNP-Glc as substrate. The enzyme activity was optimized at pH 5.0, 35°C, 2 or 6 U/ml. The recombinant β -glucosidase was immobilized to magnetic Fe₃O₄ nanoparticles. Furthermore, the optimal conditions for the immobilization and some characteristics of immobilized enzyme were studied. The optimal immobilization conditions observed were enzyme 0.15 mg (1 mg/mL, 0.15 mL), magnetic Fe₃O₄ nanoparticles 3 mg, pH 5.0, immobilization time 4 h. The results showed that the optimal reaction temperature of immobilized enzyme kept in a high activity from 35°C to 40°C. Thermal stability of the immobilized enzyme also had an improvement, the residual activity retained 62% and 57% after 180 h at 35°C and 40°C, respectively, while free enzymes only showed 55% and 51% remnant activity at the same condition. The immobilized enzyme also exhibited good operational stability. In terms of the thermal and operational stability, the immobilized enzyme could be better used in many more applications than the free enzymes. Moreover, the enzyme exhibits strong tolerance against high substrate concentration (up to 40 g/L ginsenoside Rd) with a molar biotransformation rate of 81% within 12 h. The magnetic nanoparticle immobilized β -glucosidase from B. *breve* can biotransform major ginsenoside Rd selectively to F2 and CK, indicating a great potential in industrial application for efficient production of rare ginsenoside F2 and CK.

The study was supported by the National Natural Science Foundation of China (81874332), the China Scholarship Council (CSC201708430265, CSC201708430266 and CSC201708430267), and the Natural Science Foundation of Hunan Province (2017JJ3048, 2016JJ2037).

Mono-dispersed Multi-doped LiFePO₄/C Nanoparticles as a Cathode Material for Lithium-ion Batteries

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Ni-Co-Mn doped LiFePO₄/C has been prepared from the spent electroless nickel plating bath, ferrous oxalate and lithium carbonate. A plausible formation mechanism of the multi-doped LiFePO₄/C is proposed. XRD and Rietveld refinement confirm that Ni, Co and Mn have been successfully incorporated in the LiFePO₄/C crystal. SEM and laser particle size analyses verify that the material synthesized at 700°C for 10 h consists of narrow-distribution mono-dispersed grape-like nanoparticles. The charge-discharge tests demonstrate that the material delivers initial discharge specific capacities of 167.5, 152.3 and 116.8 mAh·g⁻¹ at 0.2 C, with the capacity retentions of 99.7%, 99.0% and 98.9% after 50 cycles at 25, 0 and -20° C, respectively.



Figure 1 A SEM image of the sample



Figure 2 Initial charge-discharge curves of the sample at 0.2 C at different temperatures.

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