Self Assembly and Molecular Electronics

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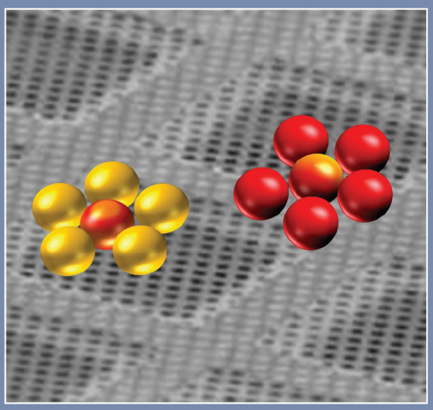

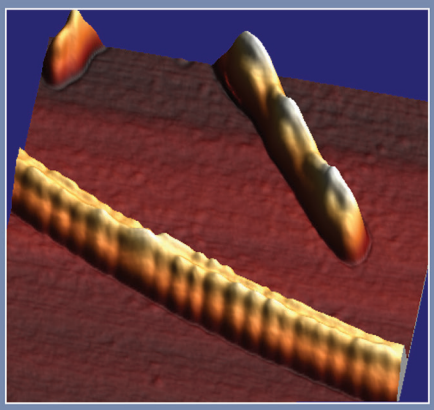

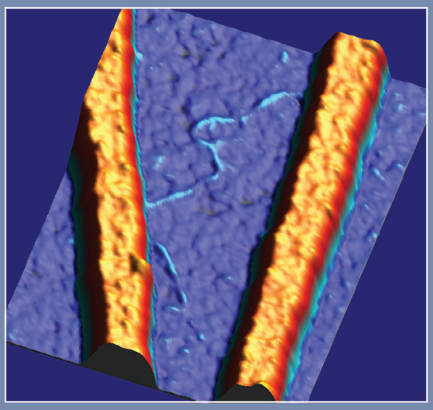

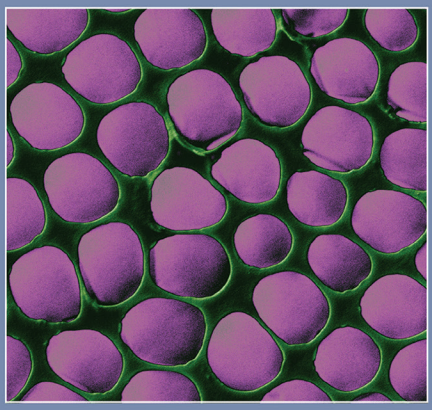

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Programme

27/08/2014

09:00 Registration and Coffee

09:55 Opening

10:00 – 10:45

Formation and transport mechanisms in individual and self-assembled networks of molecular junctions

Michel Calame

Physics Department and Swiss Nanoscience Institute, University of Basel, Basel, Switzerland
E-mail michel.calame@unibas.ch

10:45 – 11:30

First-principles modelling of charge transport in molecular junctions: Redox chemistry and quantum interference

Kristian Sommer Thygesen

Technical University of Denmark, Lyngby, Denmark
E-mail thygesen@fysik.dtu.dk

11:30 – 12:15

Gas-phase spectroscopy of donor-acceptor chromophore ions

Steen Brøndsted Nielsen

Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark
E-mail sbn@phys.au.dk

12:15 – 13:15 Lunch

13:15 – 14:00

Hybrid Materials Engineered from Bacteriorhodopsin and Semiconductor Quantum Dots or Metal Nanoparticles: What Nano Does with Bio?

Igor Nabiev[1,2,*]

[1)] *Laboratoire de Recherche en Nanosciences, LRN-EA4682, Université de Reims Champagne-Ardenne, 51100 Reims, France*
[2)] *Laboratory of Nano-Bioengineering, National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 115409 Moscow, Russian Federation*
*)*E-mail igor.nabiev@gmail.com; www.lnbe.mephi.ru*

14:00 – 14:45

Resonant and non-resonant plasmonic nanostructures

Thomas Søndergaard

Department of Physics and Nanotechnology, Aalborg University, Skjernvej 4A, DK-9220 Aalborg Øst, Denmark

14:45 – 15:20

Supported silver clusters as nanoplasmonic transducers for protein sensing

V. N. Popok[1,*], P. Fojan[1], M. Hanif[1], S. Bartling[2], I. Barke[2] and K. -H. Meiwes-Broer[2]

[1)] *Aalborg University, Aalborg, Denmark*
[2)] *Rostock University, Rostock, Germany*
*)*E-mail vp@nano.aau.dk*

15:20 – 15:45

Electrical and Optical Properties of Self-Assembled Porous Alumina Structures Filled with Iodine Nanoparticles

Vladimir Solovyev, Natalia Alekseeva, Grigory Cema and Victor Veisman

Department of Physics, Faculty of Physics and Mathematics, Pskov University, Lenin Square 2, 180000 Pskov, Russia

15:45 – 16:10

Three Dimensional Plasmonic nanostructures for Few Molecule Surface Enhanced Raman Scattering

Manohar Chirumamilla[1,2,*], Anisha Gopalakrishnan[2], Andrea Toma[2], Remo Proietti Zaccaria[2], Roman Krahne[2]

[1)] *Physics and Nanotechnology Department, Aalborg University, Aalborg, Denmark*
[2)] *Department of Nanostructures, Italian Institute of Technology, Genoa, Italy*
*)*E-mail mch@nano.aau.dk*

16:10 – 16:45 Coffee break

16:45 – 17:30

Bacterial Micro-cables and Nanowires

Andreas Bøggild[1], Manuela Gorgel[1], Jakob Jensen Ulstrup[1], Jesper Tartaru Bjerg[2], Karen Elena Thomsen[3], Lars Peter Nielsen[2], Poul Nissen[1], and Thomas Boesen[1,*].

[1)] *Department of Molecular Biology and Genetics, Aarhus University, Gustav Wieds Vej 10c, 8000 Aarhus C, Denmark.*
[2)] *Department of Bioscience, Aarhus University, Ny Munkegade 114-116, 8000 Aarhus C, Denmark.*
[3)] *iNANO, Aarhus University, Gustav Wieds Vej 14, 8000 Aarhus C, Denmark.*
*) *E-mail thb@mb.au.dk*

17:30 – 18:05

In situ obtaining water condensation by thermally controlled atomic force microscopy

Mingdong Dong

Interdisciplinary Nanoscience Center (iNANO), Centre for DNA Nanotechnology (CDNA), Aarhus University, DK 8000 Aarhus C, Denmark.
E-mail: dong@inano.au.dk

18:05 – 18:30

Surface Charge Mapping with a Nano-pipette

Lasse Hyldgaard Klausen[1,*], Flemming Besenbacher[1], and Mingdong Dong[1]

[1)] *Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus, Denmark*
**)lassehyldgaard@inano.au.dk*

18:30 – 18:55

Quantitative nanomechanical mapping of tissues by dynamic atomic force microscopy

Shuai Zhang*, Flemming Besenbacher, Mingdong Dong

The Interdisciplinary Nanoscience Center, Aarhus University
The iNANO House, Gustav Wieds Vej 14, 8000 Aarhus C, Denmark
**shuai@inano.au.dk*

18:55 – 19:00 End of session and transport to dinner

19:00 Dinner

28/08/2014

09:00 – 09:45

Long range excitation transfer in DNA nanowire

Janina Wirth, Frank Garwe, Jussi Toppari[#], Ondra Stranik, Andre Csaki

Leibniz Institute of Photonic Technology Jena, Germany
[#]Jyväskylä University, Finland

09:45 – 10:30

Enzymatic synthesis of a DNA triblock copolymer composed of natural and unnatural nucleotides for preparation of a nano-gap electrode

Kuniharu Ijiro[1,*], Hideyuki Mitomo[1], Yukie Watanabe[2], Yasunobu Suzuki[3], Yasutaka Matsuo[1], and Kenichi Niikura[1]

[1)]*Research Institute for Electronic Science, Hokkaido University, Sapporo, Japan*
[2)]*Graduate School of Science, Hokkaido University, Sapporo, Japan*
[3)]*Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Japan*
**)E-mail ijiro@poly.es.hokudai.ac.jp*

10:30 – 11:00 Coffee break

11:00 – 11:35

Controlled Deposition of Biomolecules on Solid Surfaces and Between Electrodes

Alexander Kotlyar[*,1], Gennady Eidelshtein[1], Leonid Gurevich[2] and Mohtadin Hashemi[3]

[1)]*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 69978, Israel*
[2)]*Institute of Physics and Nanotechnology, Aalborg University, 9220 Aalborg East, Denmark*

[3)] *Department of Pharmaceutical Sciences, College of Pharmacy University of Nebraska, Omaha, NE USA*
**)s2shak@post.tau.ac.il*

11:35 – 12:00

Enzymatic Activity on DNA Origami

Husnu Aslan[‡,1], Anders H. Okholm[‡,1], Jørgen Kjems[1] and Mingdong Dong[1,*]

[1)] *The Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus, Denmark*
‡ These authors contributed equally to this work.
**) E-mail dong@inano.au.dk*

12:00 – 13:00 Lunch

13:00 – 13:45

Self-assembling complexes based on protein-protein interactions

S. M. Deyev

Shemyakin & Ovchinnikov Institute of Bioorganic Chemistry RAS, Moscow, Russia;
Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, Russia;
e-mail: deyev@ibch.ru

13:45 – 14:10

Self-Assembly Potential of the Designer Peptide RFFFR

Morten Slyngborg, Leonid Gurevich, Peter Fojan

Department of Physics and Nanotechnology, Aalborg University, DK 9220 Aalborg

14:10 – 14:45

Effects of Nanoparticles on Protein Fibrillization

Giorgia Brancolini, Stefano Corni

CNR-NANO S3, Institute of Nanoscience, via Campi 213/A, 41100 Modena, Italy

14:45 – 15:10

Self-assembly of TMA on Ag (111); the role of coverage and surface temperature

Mahdi S. Baviloliaei*, Michele Gastaldo, Steffen Kiel and Lars Diekhöner

Department of Physics & Nanotechnology, Aalborg University, Aalborg, Denmark
)E-Mail: ms@nano.aau.dk

15:10 – 15:35

Visible Influence of Halogen-bonding on Supramolecular Self-assembled Nanostructures Utilizing dibenzo[fg,op]tetracene-5,6,12,13-tetracarbonitrile and 2,9-dibromidibenzo[fg,op]tetracene-5,6,12,13-tetracarbonitrile as building blocks

Huiling Zhao[1,2], Bo Liu[2], and Mingdong Dong[1,*]

[1)] *Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus C, Denmark*
[2)] *School of Physics and Electronics, Henan University, Kaifeng, China*
)E-maildong@inano.au.dk

15:35 – 16:00 Coffee break

16:00 – 16:45

Lab-on-chip Systems for Electrochemical Detection of Transmitter Release from Neuronal Cells

Rafael Taboryski

Technical University of Denmark, Department of Micro- and Nanotechnology
E-mail rata@nanotech.dtu.dk

16:45 – 17:20

Electronically Wired Proteins: Optimization of Structure-Function Relationships

Elena Ferapontova

Interdisciplinary Nanoscience Center (iNANO) Gustav Wieds Vej 14, Aarhus University, DK-8000 Aarhus C, Denmark
E-mail elena.ferapontova@inano.au.dk

17:20 – 17:55

Redox active proteins on gold surfaces: insights from a QM/MM approach

Laura Zanetti-Polzi[1,*], Isabella Daidone[2], Carlo A. Bortolotti[1,3] and Stefano Corni[1]

[1)] *Center S3, CNR NANO, Institute of Nanoscience, Via Campi 213/A, 41125, Modena, Italy.*
[2)] *Department of Physical and Chemical Sciences, University of L'Aquila, via Vetoio (Coppito 1), 67010,L'Aquila, Italy.*
[3)] *Department of Life Sciences, University of Modena and Reggio Emilia, Via Campi 183, 41125, Modena, Italy.*
**)E-mail laura.zanettipolzi@nano.cnr.it*

17:55 – 18:20

Electrochemical Analysis of Sequence-Specific Binding of Methylene Blue to Gold-Tethered DNA

Lászlo Kekedy-Nagy[1], Rui Campos[2], and Elena Ferapontova[3,*]

[1),2),3)] *Interdisciplinary Nanoscience Center (iNANO) and Center for DNA Nanotechnology (CDNA)*
Gustav Wieds Vej 14, Aarhus University, DK-8000 Aarhus C, Denmark
**)E-mail elena.ferapontova@inano.au.dk*

18:20 – 18:45

Nanostructured metal oxide Li ion battery anode materials: from zero dimension to three dimension

Lin Gao, Xiangru Li, Hao Hu and Ying Yu[*]

Institute of Nanoscience and Nanotechnology, College of Physical Science and Technology, Central China
Normal University, Wuhan 430079, China
**)E-mail yuying01@mail.ccnu.edu.cn*

18:45 – 18:55 Closing remarks

18:55 – 19:00 End of session and transport to dinner

19:00 Dinner

List of Speaker

Name	Affiliation
Kristian Thygesen	Technical University of Denmark, Lyngby, Denmark
Elena Ferapontova	Interdisciplinary Nanoscience Center (iNANO) and Center for DNA Nanotechnology (CDNA) Gustav Wieds Vej 14, Aarhus University, DK-8000 Aarhus C, Denmark
Alexander Kotlyar	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 69978, Israel
Laszlo Kekedy-Nagy	Interdisciplinary Nanoscience Center (iNANO) and Center for DNA Nanotechnology (CDNA) Gustav Wieds Vej 14, Aarhus University, DK-8000 Aarhus C, Denmark
Giorgia Brancolini	CNR-NANO S3, Institute of Nanoscience, via Campi 213/A, 41100 Modena, Italy
Laura Zanetti Polzi	Center S3, CNR NANO, Institute of Nanoscience, Via Campi 213/A, 41125, Modena, Italy
Sergey Deev	Shemyakin & Ovchinnikov Institute of Bioorganic Chemistry RAS, Moscow, Russia
Wolfgang Fritsche	Leibniz Institute of Photonic Technology Jena, Germany
Kuniharu Ijiro	Research Institute for Electronic Science, Hokkaido University, Sapporo, Japan
Rafael Taboryski	Technical University of Denmark, Department of Micro- and Nanotechnology
Vladimir Solovyev	Department of Physics, Faculty of Physics and Mathematics, Pskov State University, Lenin Square 2, 180000 Pskov, Russia
Michel Calame	Physics Department and Swiss Nanoscience Institute, University of Basel, Basel, Switzerland

Thomas Boesen	Department of Molecular Biology and Genetics, Aarhus University, Gustav Wieds Vej 10c, 8000 Aarhus C, Denmark.
Igor Nabiev	Laboratoire de Recherche en Nanosciences, LRN-EA4682, Université de Reims Champagne-Ardenne, 51100 Reims, France
Thomas Søndergaard	Department of Physics and Nanotechnology, Aalborg University, DK 9220 Aalborg
Mahdi S. Baviloliaei	Department of Physics and Nanotechnology, Aalborg University, DK 9220 Aalborg
Manohar Chirumamilla	Department of Physics and Nanotechnology, Aalborg University, DK 9220 Aalborg
Morten Slyngborg	Department of Physics and Nanotechnology, Aalborg University, DK 9220 Aalborg
Vladimir Popok	Department of Physics and Nanotechnology, Aalborg University, DK 9220 Aalborg
Mingdong Dong	The Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus, Denmark
Lasse Hyldgaard Klausen	The Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus, Denmark
Husnu Aslan	The Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus, Denmark
Shuai Zhang	The Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus, Denmark
Huiling Zhao	The Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus, Denmark
Ying Yu	Institute of Nanoscience and Nanotechnology, College of Physical Science and Technology, Central China Normal University, Wuhan 430079, China

Abstract

27/08/2014

10:00 – 10:45

Formation and transport mechanisms in individual and self-assembled networks of molecular junctions

Michel Calame

Physics Department and Swiss Nanoscience Institute, University of Basel, Basel, Switzerland
E-mail michel.calame@unibas.ch

Nanometer scale structures embedding molecular compounds represent a versatile test-bed to investigate non-equilibrium quantum transport phenomena. We follow two experimental routes to characterize and control electronic transport in molecular junctions.

Using mechanically controllable break junctions, we investigate the interplay between local spatial ordering and electronic structure to better understand the electrical transport in molecular junctions. Spectroscopic techniques help develop a deeper insight in structure-transport correlation at the individual junction level. In this perspective, I will present recent conductance fluctuations measurements [1] as well as force [2] and IV spectroscopy characterization of molecular junctions.

Arrays of metal nanoparticles interlinked by an organic matrix have attracted a lot of interest due to their diverse electronic and optoelectronic properties. We have recently shown that nanoparticle arrays form a useful architecture to build networks of molecular junctions [3]. Here, the nanoparticles act as electronic contacts to the molecules and a molecular functionality can be used to induce an overall functionality at the array scale. Using this approach, we have built nanoparticles arrays exhibiting for instance redox [4] and optical [5] switching behaviors. The latter is made possible thanks to the excitation of surface plasmons in the nanoparticles. In this particular configuration, the molecules can easily be accessed by optical means. Nanoparticle arrays thus represent an interesting architecture opening possibilities for the

development of novel molecular scale electronic and optoelectronic devices. Their possible implementation as an information storage platform or even as computing networks thanks to a defect-tolerant architecture is currently under investigation [6].

References

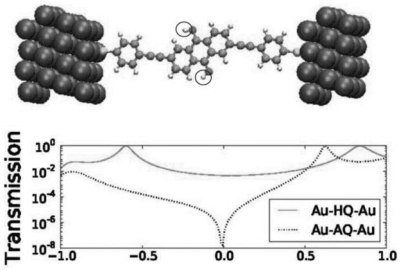
[1] J. Bruner et al., Random telegraph signals in molecular junctions, to appear in J. Phys.: Cond. Matt. (2014).
[2] C. Nef et al., Force-conductance correlation in individual molecular junctions, Nanotech., 23, 365201 (2012).
[3] J. Liao et al., Ordered nanoparticles arrays interconnected by molecular wires, submitted to Chem. Soc. Rev. (2014).
[4] J. Liao et al., Cyclic conductance switching in networks of redox-active molecular junctions, Nano Letters, 10 (3), 759–764 (2010).
[5] S. van der Molen et al., Light-controlled conductance switching of ordered metal-molecule-metal devices, Nano Letters, 9, 76–80 (2009).
[6] G. Wendin et al., Synaptic Molecular Networks for Bio-Inspired Information Processing, Int. J. Unconv. Comp., 8, 325–332 (2012).

10:45 – 11:30

First-principles modelling of charge transport in molecular junctions: Redox chemistry and quantum interference

Kristian Sommer Thygesen

Technical University of Denmark, Lyngby, Denmark
E-mail thygesen@fysik.dtu.dk



Controlling charge transport through a single molecule junction, i.e. a single molecule connected to source and drain electrodes, remains a long standing goal of molecular electronics. One way of tuning the transport properties of the molecule is to use an "electrochemical gate" thereby overcoming the technical challenges of incorporating gate electrodes for solid-state molecular devices. For redox active molecules, this approach can be used to switch between different redox states of a molecule. Of particular interest are then molecules exhibitng large differences in their transport properties between different redox states. I will discuss how the concept of quantum intereference [1], i.e. the complete or partial cancellation of the electron wave function due to phase difference between different paths through the molecule, can be exploited to realize molecular switches with on/off conductance ratios of several orders of magnitude. In particular, anthraquinone-based molecular junctions which are cross conjugated in the oxidized form and linearly conjugated in their reduced form are interesting candidates for such applications [2, 3]. Another way to tune, or at least influence, transport properties is by varying the electrode material. While most experiments to date have used Au electrodes due to their high stability, electrochemical control can be used to stabilize other types of metals which would otherwise oxidize. I will show how Ni electrodes can (i) yield better (and qualitatively different) contacts to bipyridine than Au and (ii) lead to highly spin polarized currents through the molecule, i.e. a spin filter. If time allows I will discuss the different but related problem of optimizing dyes for dye sensitized solar cells (DSSC). Our recent computational screening strategy has enabled us to build a library over the atomic structure, orbital shapes and energies of more than 5000 functionalized

porphyrins [4, 5]. Using the energy level alignment with the TiO_2 conduction band and the redox mediator, the optical absorption in the visible, and the energy barrier associated with the regeneration of the dye, we define a "quality factor" that allows us to score all the dyes in the configuration space. With this approach we identify known high efficiency dyes, suggest a number of new candidate dyes, and propose design strategies for improving the efficiency of DSSCs.

References

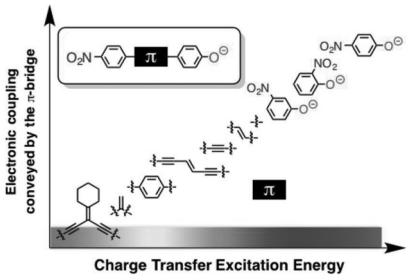
[1] T. Markussen, R. Stadler and K. S. Thygesen, Nano Lett. 10, 4260 (2010).
[2] Constant M. Guédon, Hennie Valkenier, Troels Markussen, Kristian S. Thygesen, Jan C. Hummelen, and Sense Jan van der Molen, Nature Nanotechnology 7, 305 (2012).
[3] H. Valkenier, C. M. Guédon, T. Markussen, K. S. Thygesen, S. J. van der Molen, and J. C. Hummelen, Phys. Chem. Chem. Phys. 16, 653 (2014).
[4] K. B. Oernsoe, J. M. Garcia-Lastra and K. S. Thygesen, Phys. Chem. Chem. Phys. 15, 19478 (2013).
[5] K. B. Oernsoe, J. M. Garcia-Lastra and K. S. Thygesen, Phys. Chem. Chem. Phys., accepted.

11:30 – 12:15

Gas-phase spectroscopy of donor-acceptor chromophore ions

Steen Brøndsted Nielsen

Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark
E-mail sbn@phys.au.dk



In this talk, I review our results over the last 5 years from mass spectroscopy experiments using specially designed apparatus on several charged donor-acceptor ions that are based on the nitrophenolate moiety and π-extended derivatives. These are textbook examples of donor-acceptor chromophores. The phenolate oxygen is the donor, and the nitro group is the acceptor. The choice of this system is also based on the fact that phenolate is a common structural motif of biochromophores and luminophores; for example, it is a constituent of the oxyluciferin anion responsible for light emission from fireflies. A presentation of the setups used for gas-phase ion spectroscopy in Aarhus is given, and I will address issues of whether double bonds or triple bonds best convey electronic coupling between the phenolate oxygen and the nitro group, the significance of separating the donor and acceptor spatially, the influence of cross-conjugation *versus* linear conjugation, and along this line *ortho versus meta versus para* configuration, and not least the effect of a single solvent molecule (water, methanol, or acetonitrile). From systematic studies, a clear picture has emerged that has been supported by high-level calculations of electronically excited states. Our work shows that CC2 coupled-cluster calculations of vertical excitation energies are within 0.2 eV of experimental band maxima, and importantly, that the theoretical method is excellent in predicting the relative order of excitation energies of a series of nitrophenolates. The molecular ions that have been studied are shown on the figure below in the order of increasing charge-transfer excitation energy. The results were recently reviewed in Accounts of Chemical Research [1]. Finally, I will discuss future challenges such as

following the change in absorption as a function of the number of solvent molecules and when gradually approaching the bulk limit.

Reference

[1] S. Brøndsted Nielsen, M. Brøndsted Nielsen, A. Rubio, *Acc. Chem. Res.* **47**, 1417–1425 (2014).

13:15 – 14:00

Hybrid Materials Engineered from Bacteriorhodopsin and Semiconductor Quantum Dots or Metal Nanoparticles: What Nano Does with Bio?

Igor Nabiev[1,2,*]

[1)] *Laboratoire de Recherche en Nanosciences, LRN-EA4682, Université de Reims Champagne-Ardenne, 51100 Reims, France*

[2)] *Laboratory of Nano-Bioengineering, National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 115409 Moscow, Russian Federation*

*)*E-mail igor.nabiev@gmail.com; www.lnbe.mephi.ru*

Semiconductor or metal nanocrystal self-assembly on, or their chemical attachment to, photosensitive biological systems (purple membranes of the bacterium *Halobacterium salinarum* or photosynthetic reaction centers) may strongly affect biological functions and cause plenty of interesting linear and non-linear photophysical effects on the nano-bio interface [1–3].

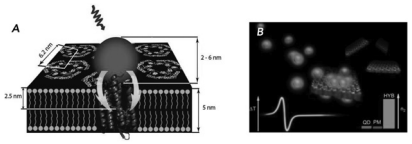


Figure 1 Self-assembly of colloidal semiconductor quantum dots (QDs, red spheres) and purple membranes (PMs, planar purple structures) in a solution: the two components are drawn to scale.

We report on the procedure of careful self-assembling of semiconductor fluorescent nanocrystals or "quantum dots" (QDs) [4] on the surface of a purple membrane (PM) of *H. salinarum* in a manner permitting Förster resonance energy transfer (FRET) from the QDs to retinal, the fluorophore of bcteriorhodopsin (bR), with an efficiency as high as 100% (Figure 1A) [5]. Additionally, we report on an enormous, wavelength-dependent enhancement of the nonlinear refractive index of wild-type bacteriorhodopsin in the presence of semiconductor QDs (Figure 1B). The effect is the strongest in the region immediately below the absorption edge of both constituents of this hybrid material and in samples that exhibit strong FRET. We have shown that enhancements of up to 4000% can be achieved by controlled the engineering of the hybrid structure, including variation of the molar ratio between the constituents.

Panel A. A semiconductor nanoparticle assembled with a bacteriorhodopsin trimer on the PM surface and optically coupled with the retinal in

order to achieve efficient FRET from the nanoparticle to the retinal. Adapted from Refs. 2 & 5.

Panel B. The nonlinear properties of QD-PM samples measured by the Z-scan technique: the yellow "butterfly" curve is a representative Z-scan curve. It has been found that, upon assembly of QD-PM complexes, the amplitude of the nonlinear refractive index (n_2) of the material is increased up to 4000% (as shown diagrammatically in the bottom right corner). Adapted from Ref. 6.

Finally, we have demonstrated that semiconductor or metal nanoparticles with different surface functionalities can be employed to control the parameters of the bR photocycle. We have shown that the lifetime of the intermediate M-form of the bR photocycle may be significantly increased when the PM is tagged with semiconductor or silver nanoparticles with desired surface charges. These new hybrid materials based on complexes of PMs with nanoparticles with unique photochromic, energy transfer, energy conversion and nanophotonic properties may be used in numerous optoelectronic applications [7]. The last but not least part of this report deals with the issues of nanomaterial toxicity resulting from the basic molecular mechanisms of interactions between nano- and biomolecular systems [8].

References

[1] I. Nabiev, A. Rakovich, A. Sukhanova, E. Lukashev, V. Zagidullin, V. Pachenko, Y. Rakovich, J. F. Donegan, A. B. Rubin, A. O. Govorov, Fluorescent quantum dots as artificial antennas for enhanced light harvesting and energy transfer to photosynthetic reaction centers. ***Angew. Chem. Intl Ed.*** **49**, 7217–7221 (2010).

[2] A. Rakovich, A. Sukhanova, E. Lukashev, V. A. Oleinikov, M. Artemyev, N. Gaponik, N. Bouchonville, M. Molinari, M. Troyon, Y. P. Rakovich, J. F. Donegan, I. Nabiev, Resonance energy transfer improves the biological function of bacteriorhodopsin within a hybrid material built from purple membranes and semiconductor quantum dots. ***Nano Lett.*** **10**, 2640–2648 (2010).

[3] A. Rakovich, J. F. Donegan, V. A. Oleinikov, M. Molinari, A. Sukhanova, I. Nabiev, Yu. P. Rakovich, Linear and nonlinear optical effects induced by energy transfert from semiconductor nanoparticles to photosensitive biological systems. ***J. Photochem. Photobiol. C: Photochem. Rev.*** **20**, 17–32 (2014).

[4] P. Samokhvalov, M. Artemyev, I. Nabiev, Basic principles and current trends in colloidal synthesis of highly luminescent semiconductor nanocrystals. ***Chemistry - A European Journal*** **19**, 1534–1546 (2013).

[5] N. Bouchonville, A. Le Cigne, A. Sukhanova, M. Molinari, I. Nabiev, Nano-biophotonic hybrid materials with controlled FRET efficiency engineered from quantum dots and bacteriorhodopsin. ***Laser Phys. Lett.*** **10**, 085901 (2013)

[6] A. Rakovich, I. **Nabiev, A.** Sukhanova, V. Lesnyak, N. Gaponik, Yu. P. Rakovich, J. F. Donegan, Large enhancement of nonlinear optical response in a hybrid nanobiomaterial consisting of bacteriorhodopsin and cadmium telluride quantum dots. ***ACS NANO*** **7**, 2154–2160 (2013).

[7] S. Yu. Zaitsev, D. O. Solovyeva, I. Nabiev, Monolayers of membrane proteins and hybrid nanostructures. ***Adv. Coll. Interf. Sci.*** **183–184**, 14–29 (2012).

[8] A. Shemetov, I. Nabiev, A. Sukhanova, Nano-bio interactions of proteins and peptides with nanocrystals. ***ACS NANO*** **6**, 4585–4602 (2012).

14:00 – 14:45

Resonant and non-resonant plasmonic nanostructures

Thomas Søndergaard

Department of Physics and Nanotechnology, Aalborg University, Skjernvej 4A, DK-9220 Aalborg Øst, Denmark

This talk will give a survey of some of the research on plasmonic nanostructures carried out at Aalborg university on resonant and non-resonant plasmonic nanostructures. Theoretical and experimental results will be presented for a non-resonant broadband absorber known as plasmonic black gold, which is a periodic array of ultra-sharp grooves with a depth of app. 500 nm and period 250 nm in a metal surface fabricated by focused-ion-beam milling. While a gold surface is usually shiny and highly reflecting the structured gold surface is a broad-band absorber and thus a black surface. This occurs because incident light is coupled into gap-plasmon polaritons (gap-SPPs) that propagate in the gap between groove walls towards the groove bottom. By using an adiabatic taper design the reflection of gap-SPPs can be avoided to a large extent. This leads to nanofocusing of light near the groove bottom. At the same time a very narrow groove near the bottom results in large absorption of gap-SPPs and as a result very small reflection. Results will also be presented for plasmonic metal nano-strip resonators including their resonance condition, resonant fields and field enhancements.

14:45 – 15:20

Supported silver clusters as nanoplasmonic transducers for protein sensing

V.N. Popok[1,*], P. Fojan[1], M. Hanif[1], S. Bartling[2], I. Barke[2] and K.-H. Meiwes-Broer[2]

[1)] *Aalborg University, Aalborg, Denmark*
[2)] *Rostock University, Rostock, Germany*
*)*E-mail vp@nano.aau.dk*

Transducers for optical sensing of proteins are prepared using silver cluster beam deposition on quartz substrates. Surface plasmon resonance phenomenon of the supported silver nanoparticles is used for the detection. Schematic picture of the sensing approach is shown in Figure 1. It is found that appropriate functionalization of quartz surface and surfaces of clusters are among the key issues for stability of clusters and protein immobilization. These procedures have been optimised. Conditions for coupling of the antibodies to the clusters are developed providing an enhancement of the plasmon absorption band used for the detection. Atomic force microscopy study allows to suggest that immobilization of antibodies on the supported silver nanoparticles has been achieved, thus giving a possibility to incubate and detect an antigen of interest (chicken egg albumin). It is shown that the compliance with the

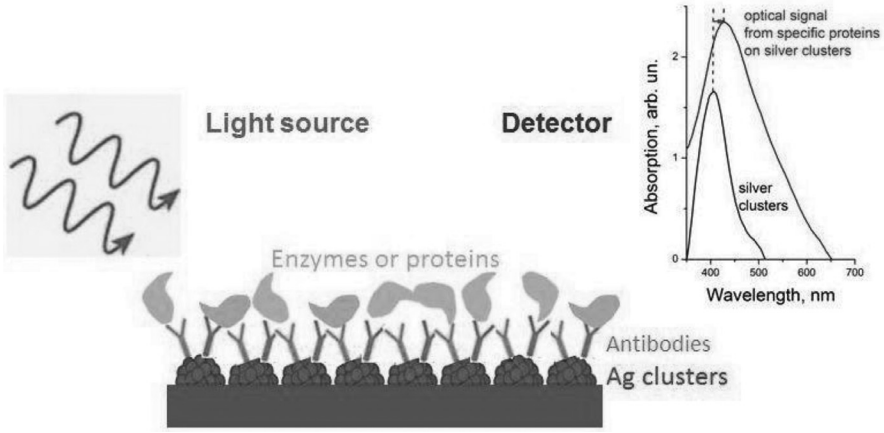


Figure 1 Schematic picture of protein detection

appropriate preparation and immobilization scheme is essential for sensitive optical detection of particular proteins. Thus, by applying the correct protocol the sensing of proteins of interest can be assured using relatively simple optical spectroscopy method.

15:20 – 15:45

Electrical and Optical Properties of Self-Assembled Porous Alumina Structures Filled with Iodine Nanoparticles

Vladimir Solovyev, Natalia Alekseeva, Grigory Cema and Victor Veisman

Department of Physics, Faculty of Physics and Mathematics,
Pskov University, Lenin Square 2, 180000 Pskov, Russia

Recently porous anodic alumina ($\mathrm{por}\ Al_2O_3$) has become a popular template system for the synthesis of various nanostructures. In this work physical properties of $\mathrm{por}\ Al_2O_3$ host matrix filled with iodine guest substance ($\mathrm{I/por}\ Al_2O_3$ nanocomposite) were studied.

Self-assembled porous alumina structures were prepared by two-step anodization process. Firstly, aluminium sheet was degreased and polished. Then anodization was performed at 40 V in 0.3M oxalic acid at $8^\circ\mathrm{C}$ for 5 h. After that the oxide layer was chemically removed. The second anodization step was performed for 5.5 h under the same conditions.

To incorporate iodine species into quasi one - dimensional parallel nanochannels of $\mathrm{por}\ Al_2O_3$ host matrix, vapour phase adsorption at $175^\circ\mathrm{C}$ under iodine vapour pressure $\sim 140\ \mathrm{kPa}$ for 7 h was used, resulting in the $\mathrm{I/por}\ Al_2O_3$ nanocomposite formation.

Dielectric measurements of the $\mathrm{I/por}\ Al_2O_3$ samples were carried out at the frequency of 1 kHz by an E7–13 impedance meter upon continuous warming with a heating rate of $\sim\ 1^\circ\mathrm{C}\ /\mathrm{min}$. Spectra of ellipsometric parameters $\Psi(\lambda)$ and $\Delta(\lambda)$ of the samples under study were characterized by the spectroscopic ellipsometer "Ellips-1891".

The measured conductivity G and capacity C values of the $\mathrm{I/por}\ Al_2O_3$ nanocomposite are 10^2 or 10^3 times larger than those of the host matrix. Their temperature dependences G(T) and C(T) demonstrate peculiarities at $\sim 70^\circ\mathrm{C}$. This temperature was previously attributed to the phase transition of iodine species in the one-dimensional nanochannels of AFI zeolite-like nanoporous aluminophosphate from the chain structures to molecular iodine.

According to our ellipsometric data, $\mathrm{por}\ Al_2O_3$ film thickness is $\sim 10\ \mathrm{microns}$. There exists a marked difference $\Delta n\ \approx\ 0.25$ between the effective refractive index of the $\mathrm{I/por}\ Al_2O_3$ nanocomposite and that of the $\mathrm{por}\ Al_2O_3$ matrix in the visible spectrum.

In summary, novel $\mathrm{I}/\mathrm{por}\ Al_2O_3$ nanocomposite prepared by infiltration of $\mathrm{por}\ Al_2O_3$ matrix with iodine guest substance was characterized by electrical and optical measurements. Experimental results prove the occurrence of the phase transition of iodine species from the chain structures to molecular iodine at $\sim 70^\circ\mathrm{C}$.

15:45 – 16:10

Three Dimensional Plasmonic nanostructures for Few Molecule Surface Enhanced Raman Scattering

Manohar Chirumamilla[1,2,*], Anisha Gopalakrishnan[2], Andrea Toma[2], Remo Proietti Zaccaria[2], Roman Krahne[2]

[1)] *Physics and Nanotechnology Department, Aalborg University, Aalborg, Denmark*
[2)] *Department of Nanostructures, Italian Institute of Technology, Genoa, Italy*
*)*E-mail mch@nano.aau.dk*

Plasmonic nanostructures[1−4] endowed with sharp tips or edges arranged in the sub-10 nm regime attained great interest in several fields, biosensing, photonics, etc. Particularly in sensing applications, Surface Enhanced Raman Spectroscopy (SERS) on metal nanostructured substrate has been increasingly utilized as an analytical technique for significant molecule detection. Using noble metal nanostructured substrates, SERS allows the detection of molecules with low concentrations down to the attomolar (10^{-18}M). Herein, we report complex 3D star-shaped nanostructures (Figure 1a)[1] with multiple tips that are decoupled from the substrate by means of standing silicon pillars. The main advantage of star shape over other geometries is that the multiple branches ensure narrow tips in the dimer (i.e., strong field confinement). Furthermore, we report nanostar dimer coupled in a ring structure (Figure 1b)[4] for highly enhanced local electric fields and recyclable SERS applications. Using these nanostructures, we report on the Raman signal originating from different kinds of biomolecules at very low concentrations (∼1 fM).

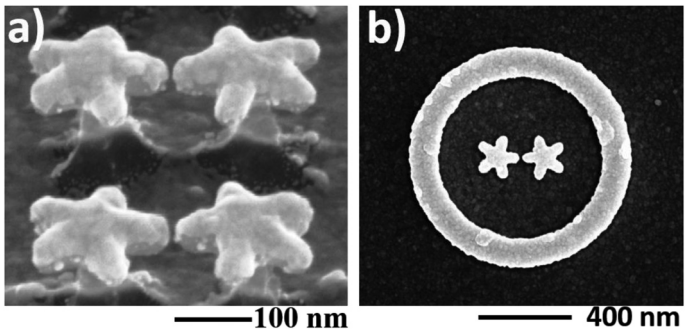


Figure 1 a) Nanostar dimer with sub-10 nm gap. b) Nanostar dimer in ring structure

References

[1] M. Chirumamilla, A. Toma, A. Gopalakrishnan, G. Das, R. P. Zaccaria, R. Krahne, E. Rondanina, M. Leoncini, C. Liberale, F. De Angelis, E. Di Fabrizio, Adv. Mat. 26, 2353–2358 (2014).

[2] M. Chirumamilla, G. Anisha, A. Toma, R. P. Zaccaria, R. Krahne Nanotechn, 25, 235303 (2014).

[3] M. Chirumamilla, G. Das, A. Toma, A. Gopalakrishnan, R. P. Zaccaria, C. Liberale, F. De Angelis, E. Di Fabrizio, Microelectron. Eng. 97, 189–192 (2012).

[4] M. Chirumamilla, G. Anisha, F. De Angelis, A. Toma, R. P. Zaccaria, R. Krahne, ACS Nano, To be Published.

16:45 – 17:30

Bacterial Micro-cables and Nanowires

Andreas Bøggild[1], Manuela Gorgel[1], Jakob Jensen Ulstrup[1], Jesper Tartaru Bjerg[2], Karen Elena Thomsen[3], Lars Peter Nielsen[2], Poul Nissen[1] and Thomas Boesen[1,*].

[1)] *Department of Molecular Biology and Genetics, Aarhus University, Gustav Wieds Vej 10c, 8000 Aarhus C, Denmark.*
[2)] *Department of Bioscience, Aarhus University, Ny Munkegade 114–116, 8000 Aarhus C, Denmark.*
[3)] *iNANO, Aarhus University, Gustav Wieds Vej 14, 8000 Aarhus C, Denmark.*
**)E-mail thb@mb.au.dk*

The discovery of bacterial nanowires, cable-like structures conductive over micrometer distances, has now intrigued many scientists for a decade [1]. The nanowires were observed in metal-reducing bacteria such as *Geobacter sulfurreducens* and *Shewanella oneidensis* and they enabled the bacteria to transfer electrons from the cell surface to extracellular electron acceptors such as insoluble metal oxides over micrometer distances or in long-range cell-cell networks in biofilms. The nanowires were proposed to be pilus-based as the *G. sulfurreducens* nanowires were found to be composed of the type IV pilin subunit PilA (Figure 1A). Furthermore, multiheme c-type cytochromes were shown to interact with the nanowire pili and based on these observations two hypotheses for electron conduction in nanowires were proposed. One of these (termed the multistep hopping or MSH hypothesis) suggested that the pilus would serve as a scaffold for highly ordered attachment of multiheme cytochromes. Based on this electron conduction could be carried out by electron 'hopping' between heme groups inside cytochromes and between adjacent cytochromes. The other (termed the metallic-like conductivity or MLC hypothesis) claimed that the pilus itself had the electron conductive properties and that the attached cytochromes were used for transfer of electrons from the pilus to the final electron acceptor. So far a number of experimental studies aimed at verifying either hypothesis have not been conclusive [2].

Recently, a novel type of bacterial long distance electron transport was proposed. The basis for this was observation of H_2S oxidation in the anoxic zone coupled with O_2 reduction in the oxic zone of seabed sediments [3]. These redox reactions were observed to be coupled over distances of centimeters

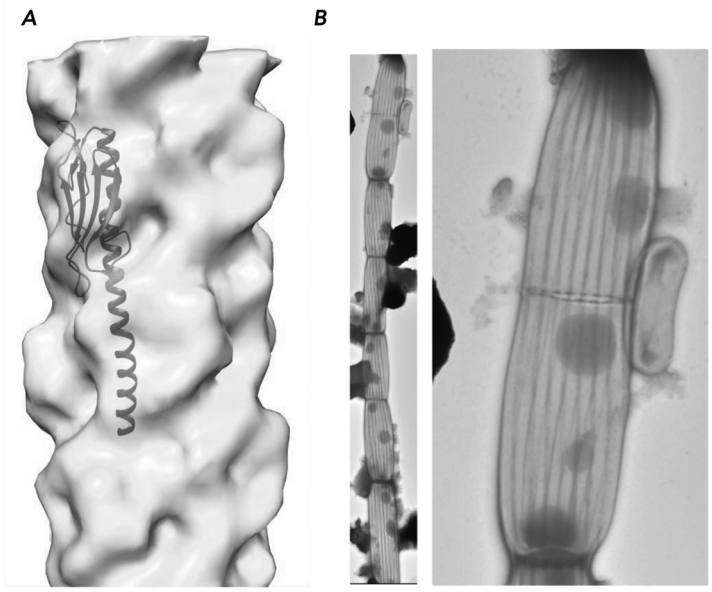


Figure 1 A: Cartoon representation of the P. aeruginosa PAK pilin structure (red) docked into the cryoelectron microscopy density map (yellow) of the type IV pilus of Neisseria gonorrhoeae to show the subunit building blocks in the pilus fiber. The diameter of the pilus is 50 A and the fiber can be several micrometers long (based on PDB entries 2HIL and 10QW, as well as EMDB entry 1236.). B: Transmission electron microscopy at 11,000 x magnification of micro-cable bacteria stained with uranyl acetate. Dark lines are observed indicating fiber structures extending from one cell to the next through hubs at the cell-cell junctions and division septa. Left image is composite image from multiple micrographs showing cells of a micro-cable filament. Right image is close up showing cell division septum and cell-cell junction.

between the O_2 and H_2S reservoirs. Examination of the sediments revealed a novel form of filamentous bacteria having a very intriguing morphology [4]. On the surface of the bacteria multiple cable-like structures were observed to extend along the length of the individual cells. Surprisingly, these cable-like structures were shared between cells and they formed continuous structures along the entire length of the bacterial filament consisting of thousands of cells and being centimeters long (Figure 1B). It was therefore suggested that electron transport was taking place inside these structures thereby coupling the redox reactions. The molecular basis for this electron transport is currently not clear.

We have engaged structural and functional studies of these amazing bioelectrical wires at the molecular level to get a firm understanding of the

underlying supramolecular organization and conduction mechanism and the status for this work will be presented.

References

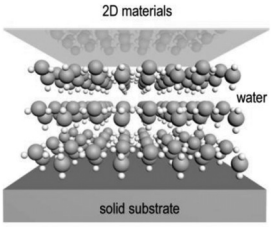
[1] G. Reguera, K. D. McCarthy, T. Mehta, J. S. Nicoll, M. T. Tuominen, D. R. Lovley. *Nature* **435**, 1098–101 (2005).
[2] T. Boesen and L. P. Nielsen. *MBio* **4**, 1–3 (2013).
[3] L. P. Nielsen, N. Risgaard-Petersen, H. Fossing, P. Bondo Christensen, M. Sayama. *Nature* **463**, 1071–4 (2010).
[4] C. Pfeffer, S. Larsen, J. Song, M. Dong, F. Besenbacher, R. L. Meyer, K. U. Kjeldsen, L. Schreiber, Y. A. Gorby, M. Y. El-Naggar, K. M. Leung, A. Schramm, N. Risgaard-Petersen, L. P. Nielsen. *Nature* **491**, 218–21 (2012).

17:30 – 18:05

In situ obtaining water condensation by thermally controlled atomic force microscopy

Mingdong Dong

Interdisciplinary Nanoscience Center (iNANO), Centre for DNA Nanotechnology (CDNA), Aarhus University, DK 8000 Aarhus C, Denmark.
E-mail: dong@inano.au.dk



Water is an interesting type of matter. Natural hydrometeor, such as rain, snow and other participation products of the water condensation, is everywhere, and, yet, the understanding of its initial stage at a surface is still unclear. At an interface of solid or confined between two solid interfaces, water vapor will precipitate. It will be extremely important to investigate the water state and the formation of water thin film on surfaces. It is a very hot topic in water science these years; water has been extensively investigated under vacuum, ambient, humility and low temperature. However an important study at each given temperature, which is to directly visualize the dynamic transition and the growth of water, is rare. It would gain a lot of interest if thermal responds could be introduced and develop a new and more accurate method for the analysis of water phase transition and growth under ambient conditions. Herein, we investigate the condensation of water vapor occurred in both hydrophobic-hydrophilic interface and hydrophilic-hydrophilic interface via *in situ* thermally controlled atomic force microscopy Our work presents the first demonstration of the recently developed thermally controlled atomic force microscopy allowing to visual water adlayer growth before transition to water liquid state. By introducing the new measurement performed in ambient conditions at each give temperature, we confirm the theoretical finding. For the first time, we are able to visualized three ice-like water adlayer growth before transition to liquid droplet. The initial stage of the hydrometeor was rationalized.

References

[1] Evidence of Stranski–Krastanov growth at the initial stage of atmospheric water condensation

Jie Song, Qiang Li, Xiaofeng Wang, Jingyuan Li, Shuai Zhang, Jørgen Kjems1, Flemming Besenbacher, Mingdong Dong* Nature Communications 2014. DOI: 10.1038/ncomms5837

[2] Two-dimensional materials confined water
Qiang Li, Jie Song, Flemming Besenbacher, Mingdong Dong Accounts of Chemical Research 2014 (inivted review)

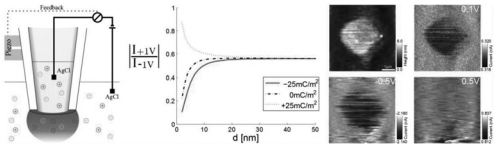
18:05 – 18:30

Surface Charge Mapping with a Nano-pipette

Lasse Hyldgaard Klausen[1,*], Flemming Besenbacher[1], and Mingdong Dong[1]

[1)] *Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus, Denmark*

**)lassehyldgaard@inano.au.dk*



Surface charges in a biological system are molecules exposing ionic charges to the surrounding media. The surface charges form a local electrostatic environment that rejects particles of like charge and attracts particles of opposite charge. Mammalian cell membranes are composed of a mixture of lipids and proteins; these form a unique pattern of surface charges that guide cell-cell interactions and the uptake of charged particles [1]. The surface charge pattern is fluctuating and characterising it has however proven a challenging task. Here we introduce a new method for measuring surface charges based on the Scanning Ion-Conductance Microscope [2]. In the SICM setup (figure 1A), the ionic current through a nano-pipette is used to detect surface topography from an occlusion of the tip area, as the pipette is moved towards a sample surface. We have recently presented a one nanometre vertical resolution for the imaging of biological materials [3], and we have been working on improving the method to enable the measurement of surface charges. We have found that the ionic concentration in the nano-pipette apex is slightly affected by surface charges on the sample (figure 1A, B). This accumulation of ions can be tuned by applying a varying current, and by using this we have developed a method to characterise the surface charge. In our work we apply a theoretical approach by solving Poisson and Nernst-Planck equations to support the method, and we report the experimental mapping of surface charges on a well-defined sample [4]. We believe that this new method will be a great asset especially for the characterisation of model.

References

[1] Z. Korade, A. K. Kenworthy, *Neuropharmacology* 55(8), 1265–1273 (2008).

[2] P. K. Hansma, B. Drake, O. Marti, S. A. C. Gould, C. B. Prater, *Science* **243(4891)**, 641–643 (1989).

[3] S. Zhang, S. J. Cho, K. Busuttil, C. Wang, F. Besenbacher, M. Dong, *Nanoscale* **4(10)**, 3105–3110 (2012).

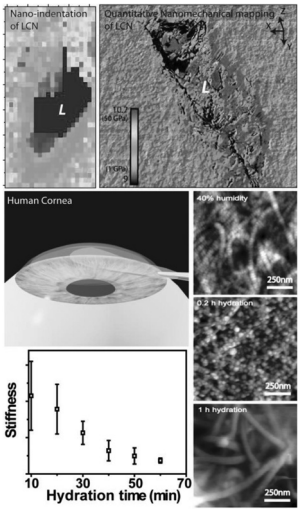
[4] L. H. Klausen, F. Besenbacher, M. Dong, *In Preparation*.

18:30 – 18:55

Quantitative nanomechanical mapping of tissues by dynamic atomic force microscopy

Shuai Zhang*, Flemming Besenbacher, Mingdong Dong

The Interdisciplinary Nanoscience Center, Aarhus University
The iNANO House, Gustav Wieds Vej 14, 8000 Aarhus C, Denmark
**shuai@inano.au.dk*



Quantitative nanomechanical mapping by dynamic atomic force microscopy (AFM) is a quite important development in nanotechnology and nanocharacterization. In biophysical field, it not only provides the opportunities to probe the topography of various biological species under physiological environment, but it also enables researchers to understand the relevant physical/chemical properties quantitatively, basing on the force measurements.[1] After more than ten-year development, such quantitative nanomechanical mapping has led to numerous discoveries in life science, such as providing the fine structures of protein self-assembly structures[2] and localizing the functional sites on cellular membrane. However, the reports of the applications on tissue level are still rare. In this presentation, we would like to share our recent applications of quantitative nanomechanical mapping to understand the roles of osteocytes and lacunar-canalicular network (LCN) in regulating bone quality and calcium homeostasis, and to figure out the hydration effects to human corneal[3].

References

[1] Zhang, S.; Aslan, H.; Besenbacher, F.; Dong, M., Quantitative biomolecular imaging by dynamic nanomechanical mapping. *Chemical Society Reviews* 2014.

[2] Zhang, S.; Andreasen, M.; Nielsen, J. T.; Liu, L.; Nielsen, E. H.; Song, J.; Ji, G.; Sun, F.; Skrydstrup, T.; Besenbacher, F.; Nielsen, N. C.; Otzen,

D. E.; Dong, M., Coexistence of ribbon and helical fibrils originating from hIAPP20–29 revealed by quantitative nanomechanical atomic force microscopy. *Proceedings of the National Academy of Sciences* 2013.

[3] Xia, D.; Zhang, S.; Hjortdal, J. Ø.; Li, Q.; Thomsen, K.; Chevallier, J.; Besenbacher, F.; Dong, M., Hydrated Human Corneal Stroma Revealed by Quantitative Dynamic Atomic Force Microscopy at Nanoscale. ***ACS Nano*** 2014.

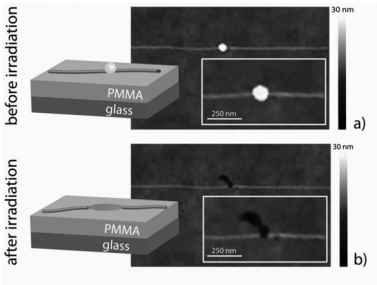
28/08/2014

09:00 – 09:45

Long range excitation transfer in DNA nanowire

Janina Wirth, Frank Garwe, Jussi Toppari#, Ondra Stranik, Andre Csaki

Leibniz Institute of Photonic Technology Jena, Germany
#Jyväskylä University, Finland



The conduction electrons of metal nanoparticles can be resonantly excited at their plasmonic frequencies in the visible wavelengths as localized surface plasmon resonance (LSPR). It results in intense scattering and absorption of light, what can be utilized for biosensing down to the single particle level.

It leads to large enhancements of the electromagnetic field near the particles. Short-pulsed (fs) laser pulse excited electrons of the nanoparticle can even couple into attached aligned molecular wires consisting of double-stranded (ds) lambda DNA.

We present studies of fs laser irradiated silver and gold nanoparticles attached to these dsDNA molecules that show that such a plasmonic excitation of the particle can couple to dsDNA and cause a long-range excitation transfer along these molecules. This was demonstrated by a micrometer long destruction of the DNA, under certain conditions even of an underlying PMMA film along these molecules. This phenomenon was studied more thoroughly by fluorescence experiments, where a fs pulse plasmonic excitation of an acceptor AgNP induced bleaching of fluorophores at a donor AgNP by excitation transport along DNA molecules, which connected both nanoparticles over a distance of 5.7 μm.

09:45 – 10:30

Enzymatic synthesis of a DNA triblock copolymer composed of natural and unnatural nucleotides for preparation of a nano-gap electrode

Kuniharu Ijiro[1,*], Hideyuki Mitomo[1], Yukie Watanabe[2], Yasunobu Suzuki[3], Yasutaka Matsuo[1], and Kenichi Niikura[1]

[1)] *Research Institute for Electronic Science, Hokkaido University, Sapporo, Japan*
[2)] *Graduate School of Science, Hokkaido University, Sapporo, Japan*
[3)] *Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Japan*
*)*E-mail ijiro@poly.es.hokudai.ac.jp*

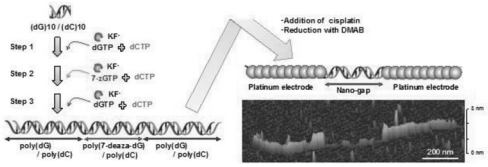


Figure 1 Fabrication of metal nanowires based on DNA-templated metallization of a DNA triblock copolymer

Nucleobase-selective metallization of DNA has been expected to enable the fabrication of nanostructured electronic devices such as a nano-gap electrode and a p-n junction by self-organization. We showed that a DNA-templated gold nanoparticle (AuNP) / polyaniline-alternated hybrid nanowire, with a configuration resembling that of a one-dimensional array of tunnel junctions, could support Coulomb blockade transport [1]. The AuNPs act as the conductor, while the polyaniline serves as the capacitor junctions, with the two components alternately aligned on DNA in a sequential assembly process.

In order to prepare conductive nanowires with natural DNA, we employed guanine N_7-binding cis-platin as the precursor of catalyst for electroless plating of λ-DNA [2]. Cis-platin bound to λ-DNA was transformed to Pt cluster by chemical reduction. After stretching the Pt-deposited λ-DNA by LB method, rapid and selective deposition of Ag on DNA was achieved upon the introduction of Ag^+ and reducing agent. This biometallization approach provided linear Ag NWs of 50–100 nm in width with high conductivity [3]. To apply sequence specificity of DNA for metal deposition, we synthesized DNA diblock copolymer composed of poly(dG)-poly(dC) (GC part) and poly (dAT) (AT part) by using the Klenow fragment exo$^-$ as the

polymerase [4]. This artificial sequence thereby allows cis-platin to selectively interact with the GC segment, other than the AT part. The reduction of cis-platin further led to a sequence-specific Pt deposition on the stretched DNA. Construction of novel tunneling nanostructures via DNA templating was explored. Reduction of cisplatin bound to guanine (G) of DNA can provide Pt nanowires. Meanwhile, 7-deaza-G is expected not to be bound to cisplatin because N_7 which binds to cis platin is changed to C_7. In this report we synthesized DNA triblock copolymers consisted of poly(dG)-poly(dC) and poly(7-deaza-dG)-poly(dC) blocks by enzymatic reactions for the preparation of nano-gap electrodes by deposition of Pt onto the poly(dG)-poly(dC) block. It is expected that the poly(7-deaza-dG)-poly(dC) block part acts as a nano-gap (Figure 1).

For that purpose DNA homopolymers such as poly(dG)-poly(dC), poly(7-deaza-dG)-poly(dC) and triblock copolymer poly(dG)-poly(dC) / poly(7-deaza-dG)-poly(dC) / poly(dG)-poly(dC) were synthesized from dG_{10} and dC_{10} as template primers using DNA polymerase Klenow fragment exo$^-$. Molecular weight of synthesized DNA polymers was measured by electrophoresis. The DNA polymers were immobilized on mica substrates by the LB method and were reacted with cis platin and reduced. Heights of the DNA polymers were measured by AFM.

About 3,000 bp of poly(dG)-poly(dC) was obtained by 1 h of polymerization reaction in the presence of dGTP and dCTP. When 7-deaza-dGTP was added instead of dGTP, 3,000 bp poly(7-deaza-dG)-poly(dC) was obtained. Poly(7-deaza-dG)-poly(dC) could be polymerized in almost the same speed of poly(dG)-poly(dC). CD spectra and Tm measurement showed that the structure of poly(7-deaza-dG)-poly(dC) was much differ from that of poly(dG)-poly(dC). By changing of the dNTPs from dGTP to 7-deaza-dGTP, triblock copolymer DNA was synthesized. After reduction of cis platin the DNA block copolymer was observed by AFM. The image showed that height of one block increased due to the deposition of platinum metal, indicating that cis platin was selectively bound to guanine, not to 7-deaza-guanine in this experimental condition. It is expected that reduction of cisplatin with the triblock copolymer can provide the nano-gap electrodes.

References

[1] G. Wang, H. Tanaka, L. Hong, Y. Matsuo, K. Niikura, M. Abe, K. Matsumoto, T. Ogawa, K. Ijiro, *J. Mater. Chem.*, **22**, 13691–13697 (2012).

[2] Y. Hashimoto, Y. Matsuo, K. Ijiro, *Chem. Lett.*, **34**, 112–113 (2005).
[3] G. Wang, A. Ishikawa, A. Eguchi, Y. Suzuki, S. Tanaka, Y. Matsuo, K. Niikura, K. Ijiro, *ChemPlusChem*, **77**, 592 (2012).
[4] A. Tanaka, Y. Matsuo, Y. Hashimoto, and K. Ijiro, *Chem. Comm.*, 4270–4272 (2008).

11:00 – 11:35

Controlled Deposition of Biomolecules on Solid Surfaces and Between Electrodes

Alexander Kotlyar[*,1], Gennady Eidelshtein[1], Leonid Gurevich[2] and Mohtadin Hashemi[3]

[1)] *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 69978, Israel*

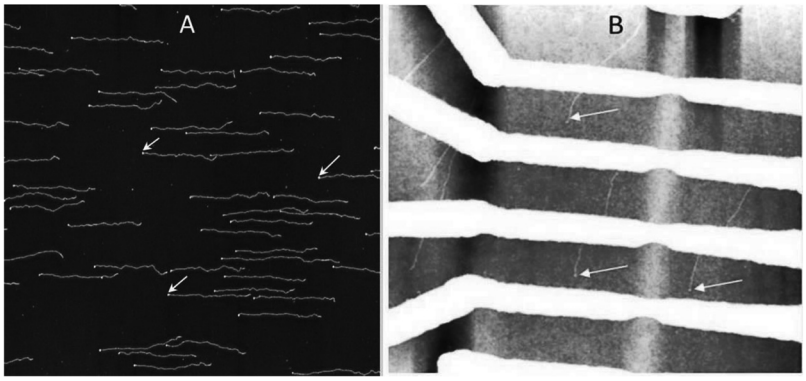
[2)] *Institute of Physics and Nanotechnology, Aalborg University, 9220 Aalborg East, Denmark*

[3)] *Department of Pharmaceutical Sciences, College of Pharmacy University of Nebraska, Omaha, NE USA*

**)s2shak@post.tau.ac.il*

Electrical measurements require controlled deposition of molecules across metal electrodes. DNA and other biomolecules (like, for example, bacteriophages) cannot bind to bare mica and silicon surfaces due to electrostatic between the substrates and the molecule. Treatment of mica with Mg-ions and silicon with aminosilanes reverses the charge of both the above surfaces from negative to positive and enables binding of negatively charged species. Strong charge-mediated interactions with the surface however may cause significant disruption of the structure of soft biomolecules and reduce their ability to conduct electrical current.

In the talk, I'll introduce a novel method for DNA deposition on non-modified mica and silicon surfaces that we have recently developed. The initial



binding to the surface occurs through the avidin molecule attached to the end of the DNA. This positively charged protein anchors the complex to mica and silicon surfaces. Drying of the surface with nitrogen yielded molecules aligned in the direction of the gas flow (left panel). Using this approach we deposited DNA across metal electrodes (right panel). Electrical conductivity measurements through these molecules are underway.

Atomic Force Microscopy image of avidin-DNA on mica (A) and crossing a gap between platinum electrodes (B). Avidin-DNA solution in 20 mM LiCl was dropped on a mica surface (A) or a silicon wafer (B). The surfaces were rinsed with double distillate water and dried by nitrogen gas. The arrows show avidin molecules attached to DNA.

11:35 – 12:00

Enzymatic Activity on DNA Origami

Husnu Aslan[‡,1], ***Anders H. Okholm***[‡,1], ***Jørgen Kjems***[1] ***and Mingdong Dong***[1,*]

[1)]*The Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus, Denmark*

‡*These authors contributed equally to this work.*

*)*E-mail dong@inano.au.dk*

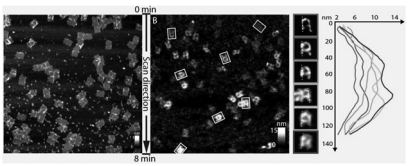


Figure 1 TM AFM in fluid height image of DNA Origami canvases in TdT buffer A) not containing BSA. No growth is observed even though TdT's surface coverage was increasing in time, B) containing BSA. Growth of nucleotide chains in the shape of letter A is observed. Color-coded line profiles comparison clearly shows the growth numerically.

Controlled surface-initiated reactions are considered an intriguing strategy to modify the chemical, physical and biological properties of surface substrates. Various natural materials have been employed to facilitate or organize reactions at bioinspired surfaces including DNA[1], RNA[2] and protein[3]. Since the development of programmable DNA nanostructures and particularly DNA origami, DNA has been the favourite choice for templating reactions with nanometer precision. DNA nanostructures have provided a versatile platform for successive strand displacement reactions[4], click chemistry reactions[5] and enzymatic reactions[6]. Recently, the intriguing potential for manipulation of DNA by the large selection of DNA-modifying enzymes has been emphasized[7]. DNA polymerases, ligases, and nucleases can be used to elongate, connect and cut DNA strands. This provides a diverse toolbox for controlling and manipulating DNA nanostructures. However, to fully appreciate the available enzymes, their interaction with complex DNA assemblies must be thoroughly investigated. Here, we have demonstrated DNA polymerase Terminal deoxynucleotidyl transferase (TdT) mediated elongation of single stranded DNA patterns on a 100 x 70 nm^2 DNA origami canvas with nanometer resolution. The DNA canvas consists of 220 pixels separated $\sim$5 nm, each being available for selective elongation. The polymerization reaction catalyzed by TdT and bovine serum albumin (BSA) was visualized in real-time using Tapping Mode AFM in liquid under ambient

conditions. We found that polymerization was promoted by BSA and recorded growth of structures of up to 50 nm. Moreover, we have observed an interesting behavior in selectivity. TdT was promoting the growth on only about half of the DNA canvases, while the rest was remaining unmodified.

References

[1] F. Ozsolak, A. R. Platt, D. R. Jones, J. G. Reifenberger, L. E. Sass, P. McInerney, J. F. Thompson, J. Bowers, M. Jarosz and P. M. Milos, *Nature*, 2009, **461**, 814–U873.
[2] S. Seetharaman, M. Zivarts, N. Sudarsan and R. R. Breaker, *Nat Biotechnol*, 2001, **19**, 336–341.
[3] G. MacBeath and S. L. Schreiber, *Science*, 2000, **289**, 1760–1763.
[4] H. Z. Gu, J. Chao, S. J. Xiao and N. C. Seeman, *Nature*, 2010, **465**, 202–U286.
[5] N. V. Voigt, T. Torring, A. Rotaru, M. F. Jacobsen, J. B. Ravnsbaek, R. Subramani, W. Mamdouh, J. Kjems, A. Mokhir, F. Besenbacher and K. V. Gothelf, *Nat Nanotechnol*, 2010, **5**, 200–203.
[6] O. I. Wilner, Y. Weizmann, R. Gill, O. Lioubashevski, R. Freeman and I. Willner, *Nat Nanotechnol*, 2009, **4**, 249–254.
[7] S. Keller and A. Marx, *Chem Soc Rev*, 2011, **40**, 5690–5697.

13:00 – 13:45

Self-assembling complexes based on protein-protein interactions

S. M. Deyev

Shemyakin & Ovchinnikov Institute of Bioorganic Chemistry RAS, Moscow, Russia;
Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, Russia;
e-mail: deyev@ibch.ru

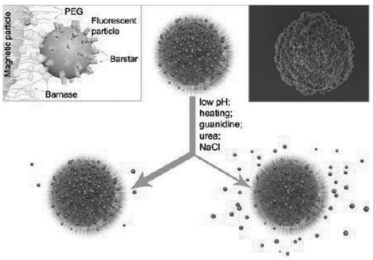


Figure Concept of multipoint contacts between the components of the colloidal assembly (left), SEM image of the barnase-barstar system assembled structure (right) and general schematic view of the self-assembly system behavior upon disassembly of the preassembled structures in protein-denaturing conditions (center).

Numerous self-assembly systems have been designed that allow for control of their behavior in terms of assembly-disassembly in different conditions by triggering these transitions with relatively gentle stimuli of various nature. For example, in nucleic acid-based systems, disassembly may be triggered upon temperature denaturation of DNA duplexes holding particles within the assembly; other examples include disassembly induced by competing oligonucleotides, lowering of pH, and divalent cations of transition metals, etc. These approaches to achieve controllability of the assemblies using various stimuli have a great potential in the construction of "smart" materials for a number of applications (drug delivery, biosensors, etc.). In this work, we address the question of stability of the barnase-barstar system (BBS) -"glued" assemblies subject to destruction. To this end, we test their behavior under severe protein denaturing conditions such as high temperature and low pH as well as high salt and chaotropic agent (urea and guanidinium hydrochloride) concentrations.

Yet in other situations it is desirable to design materials that would not readily disassemble under appropriate conditions. For example, self-assembled multifunctional theranostic agents are expected to demonstrate significant stability to ensure retention of all functional modules within a single entity to be able to perform all programmed functions (e.g., imaging, drug delivery, stimulus-responsiveness) with equal efficiency. We studied protein-assisted

nanoparticle self-assembly systems (namely, those based on barnase-barstar, streptavidin-biotin, antibody-antigen, and protein A-immunoglobulin interactions) that exhibit unexpected robustness in denaturing conditions intolerable for most proteins. Use of proteinaceous "molecular glues" for nanoparticle self-assembly purposes is of interest due to the advantages of introducing new functionalities to the self-assembled structures via additional protein modules fused to initial molecules mediating assembly. Among them, we find the barnase-barstar pair particularly noteworthy due to benefits offered by genetic engineering of this entirely protein based system and ease of heterologous prokaryotic expression of the proteins in ample amounts. The barnase-barstar system has found applications in bioengineering and design of a number of fusion proteins and supramolecular constructs. To the benefit of barnase and barstar genetic engineering, N- and C-termini of both proteins are not involved in the molecular interface of the proteins within the complex, so they are available for fusions such as those with antibodies, fluorescent proteins, and bacterial toxins, which can be used as additional functional modules of the hybrid protein-particle constructions. That distinguishes the BBS from the other above-mentioned protein-based self-assembly approaches, which are generally used per se.

Experiments show that the obtained constructs possess unusual stability and tolerate conditions far beyond physiological ones. The BBS was also compared to other widely used self-assembly systems mentioned above, in terms of resistance of the preassembled structures to the extreme conditions as well as with respect to their ability to mediate assembly of the initial conjugates involving the components of these systems. Unexpectedly, whereas in the former case the tested systems demonstrate a relatively similar behavior, their performance in the latter differs substantially.

The results on applications of barnase-barstar platform with important types of the nanoparticles, including quantum dots, luminescent nanodiamonds, colloidal gold, magnetic NPs, luminescent upconversion NPs as well as delivery of pseudomonas exotoxin A and radioisotope to the HER2/neu overexpressing human adenocarcinoma cells also are reviewed.

13:45 – 14:10

Self-Assembly Potential of the Designer Peptide RFFFR

Morten Slyngborg, Leonid Gurevich, Peter Fojan

Department of Physics and Nanotechnology, Aalborg University, DK 9220 Aalborg

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 β-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]

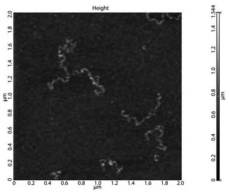


Figure 1 AFM image of fibers self-assembled from the peptide RFFFR. A peptide solution with concentration 8 mM was prepared in 1X PBS buffer and allowed to age over night. The solution was then diluted to a total concentration of 1 mM and allowing the spheres to unwrap for 40 min before incubating the solution on freshly cleaved mica for 12 min and rinsing it twice with milliQ water.

As none of these peptides form fibers resembling amyloids, we have designed a peptide that self-assembles into nano-fibers. Based on the triphenylalanine peptide we restricted the interaction of the phenylalanine residues to one direction by adding Arginine residues to both termini, yielding the peptide sequence RFFFR. The self-assembly has been investigated with circular dichroism, SEM and AFM, see Figure 1. It has been concluded that at low salt concentrations (1x PBS) this peptide forms fibers that entangle and form spheres. If the solution is diluted below the critical fiber concentration the fibers, comprising the spheres, unwrap. At higher salt concentrations (5x PBS) the fibers are stable and have an average length of several micrometers with a height of 1.4 nm. The circular dichroism response is dominated by the pi-pi interactions and is blue-shifted depending on peptide concentrations. From

circular dichroism no apparent critical peptide concentration is observed, indicating that the phenylalanine residues also interact through pi-pi interactions below the critical concentration.

Furthermore, molecular details have been investigated in a molecular dynamics study where initially a total of 27 peptides were randomly placed in a simulation box and the self-assembly was monitored by coarse-grained simulations employing the MARTINI force field[3]. The final structure was then converted to all-atom and a short simulation was performed. Amongst other things, this study reflects upon the intra- as well as intermolecular π-π interactions of phenylalanine residues and the critical fiber concentration of the peptide RFFFR.

Literatures

[1] M. Hashemi, P. Fojan and L. Gurevich, Journal of Self-Assembly and Molecular Electronics, 2013, 1, 195–208.
[2] P. Tamamis, L. Adler-Abramovich, M. Reches, K. Marshall, P. Sikorski, L. Serpell and E. Gazit, Biophysical Journal, 2009, 96, 5020–5029.
[3] M. Baaden and S. J. Marrink, Structural Biology, 2013, 23, 878–886.

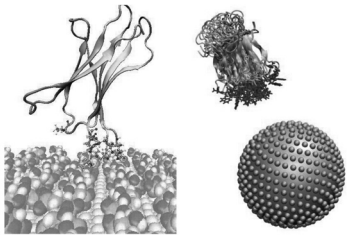
14:10 – 14:45

Effects of Nanoparticles on Protein Fibrillization

Giorgia Brancolini, Stefano Corni

CNR-NANO S3, Institute of Nanoscience, via Campi 213/A, 41100 Modena, Italy

Nanoparticles (NPs) are recognized to exhibit distinct physical and chemical properties compared with the same materials in the bulk form. [1] As they enter into biological systems, they are immediately exposed to a variety and concentration of proteins. The physico-chemical interactions between proteins and NPs are influenced by the surface chemistry of the NPs. The formation of protein-NPs complexes rather than the NPs alone, determines the resulting biological responses [2] which can affect protein function, such as fibrillogenesis. Protein fibrillation is common to many protein and it causes cerebral and systemic amyloid disease.



12.

Figure 1 Monomeric protein interacting with citrate-capped gold nanoparticle

Computer simulations at the atomistic level are a powerful tool that can effectively complement experimental studies. [3, 4] To identify the effects of NP surface chemistry on the fibrillation propensity of proteins and to interpret the hypothesis that the effect of the environment may physiologically support the deposition, [3] we perform a series of simulations by using different levels of theory (Temperature Replica Exchange MD (T-REMD) and Brownian Dynamics) that cover multiple length- and time-scales. Relevant effects of the environment on protein conformational stability are described involving: (I) protein in solution (II) protein in proximity of charge arrays e.g. gold charged surfaces (Fig.1) Chemical shifts [5] and simulations at multiple levels [6] explain the origin of the observed protein perturbations mostly localized at the aminoterminal region. The results offer possibile strategies for controlling the desired effect of NPs and their corresponding effects on the conformational changes of the proteins, which have significant roles in the fibrillation process.

References

[1] Kumar *et al.,* **2013**. Manual on Critical Issues in Nanotechnology R&D Management: An Asia-Pacific Perspective. APCTT-ESCAP.
[2] Lynch, I. *et al*., *Adv. Colloid Interface Sci.* **2007**, *134–135*, 167–174.
[3] Domanska K. *et al.* PNAS **2011**; 108:1314–1319.
[4] Linse S. *et al.* PNAS **2007**;104:8691–8696.
[5] (i) Mangione, P. P. *et al.*, *J. Biol. Chem.* **2013**, *288*, 30917–30930 (ii) G. Esposito *et al.* *Subcell Biochem*. **2012**, *65*, 165–83.
[6] (i) Brancolini, G. *et al. Nanoscale*, **2014**, DOI: 10.1039/C4NR01514B (ii) Brancolini, G. *et al.* Manuscript in preparation.

14:45 – 15:10

Self-assembly of TMA on Ag (111); the role of coverage and surface temperature

Mahdi S. Baviloliaei*, Michele Gastaldo, Steffen Kiel and Lars Diekhöner

Department of Physics & Nanotechnology, Aalborg University, Aalborg, Denmark
**)E-Mail: ms@nano.aau.dk*

Molecular self-assembly has been developed as a bottom-up nanofabrication method, using organic molecules and atoms as building blocks to fabricate structures with great precision [1]. Recently, interaction mechanisms such as hydrogen bonding and metal-organic interactions have proven to have the advantages of stability, directionality and also the formed structures are transformable to novel patterns at certain conditions [2]. Trimesic acid (TMA) has previously been studied on different noble metal surfaces [3–5]. On Ag (111) it was found that TMA deposited at room temperature form an open honeycomb network, whereas annealing to 420 K leads to a dense close-packed phase [4].

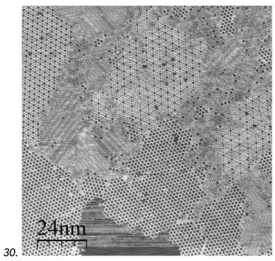


Figure 1 STM images of TMA deposited at room temperature on a Ag (111) single crystal surface. The image size is 120 nm × 120 nm. Several domains of well-ordered structures formed by self-assembly are observed.

We have used a Scanning Tunneling Microscope under ultra-high vacuum conditions to study the self-assembly of TMA on Ag(111) as a function of coverage and surface temperature.

The coverage effect is illustrated in Figure 1. In the lower part of the image the honey-comb phase is seen, whereas other parts of the surface contain domains of denser phases of well-ordered TMA molecules. It is observed that the denser phases are created by successive filling of the open pores in the honey-comb structure. The final saturation structure is completely filling the surface.

We also investigated the effect of surface temperature by annealing the surface from room temperature to 430 K in successive small steps of 25 K.

We find a rich variety of structures. The self-assembly of TMA on Ag(111) thus forms long-range ordered networks, where the shape and most likely also the properties depend strongly on both coverage and temperature.

References

[1] Kühnle, A., Current Opinion in Colloid & Interface Science, 2009. 14(2): p. 157–168.
[2] Barth, J.V., G. Costantini, and K. Kern, Nature, 2005. 437(7059): p. 671–679.
[3] Ye, Y., *et al.*, The Journal of Physical Chemistry C, 2007. 111(28): p. 10138–10141.
[4] Payer, D., *et al.*, Chemistry – A European Journal, 2007. 13(14): p. 3900–3906.
[5] Baviloliaei, M.S. and L. Diekhöner, Physical Chemistry Chemical Physics, 2014. 16(23): p. 11265–11269.

15:10 – 15:35

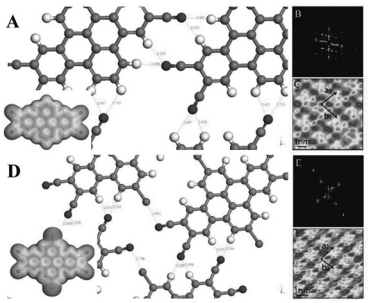
Visible Influence of Halogen-bonding on Supramolecular Self-assembled Nanostructures Utilizing dibenzo [fg, op]tetracene-5,6,12,13-tetracarbonitrile and 2,9-dibromidibenzo [fg, op]tetracene-5,6,12,13-tetracarbonitrile as building blocks

Huiling Zhao[1,2], Bo Liu[2], and Mingdong Dong[1,*]

[1)] *Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus C, Denmark*

[2)] *School of Physics and Electronics, Henan University, Kaifeng, China*

**)E-maildong@inano.au.dk*



Because of unusual charge distribution and favorable lipophilicity, halogen ligands have been extensively adopted in biological systems and supramolecular chemistry fields, for example, performing antibiotic inhibitors and drug candidates to enhance membrane penetration. Meanwhile, halogen bonds compete with coexisting hydrogen bonds to determine the functional conformations of secondary and higher-order structures of macromolecular systems. In this work, two-dimensional(2D) supramolecular networks formed respectively by two kinds of dibenzo [fg, op]naphthacene derivatives, have been investigated at liquid/solid interface through scanning tunneling microscopy(STM) technique. Comparing their high-resolution STM images, it is obvious that the halogen-bonding has a significant effect on these self-assembled nanostructures, which can be visualized at molecular level. Combined with theoretical calculation to evaluate the molecule-substrate and molecule-molecular interactions, we suggest that there is the competition existing between halogen-bonding, hydrogen-bonding and π-π interaction, and they play different roles under different conditions. This work not only intuitively exhibits that halogen bonding could play the elaborate regulating

role during the molecular self-assembly process, but also indicates the competition of multiple non-covalent interactions can affects the final molecular structures, even the physicochemical function of self-organization systems.

References

[1] M. Z. Hernandes, S. M. T. Cavalcanti, D. R. M. Moreira, de W. F. de Azevedo, A. C. L. Leite, *Curr. Drug Targets* **11**, 303–314(2010).

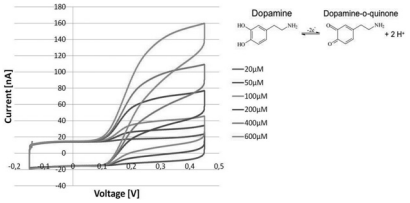
[2] J. K. Yoon, W. J. Son, K. H. Chung, H. Kim, S. Han, S. J. Kahng, *J. Phys. Chem. C* **115**, 2297–2301 (2011).

16:00 – 16:45

Lab-on-chip Systems for Electrochemical Detection of Transmitter Release from Neuronal Cells

Rafael Taboryski

Technical University of Denmark, Department of Micro- and Nanotechnology
E-mail rata@nanotech.dtu.dk



Electrochemical detection of electroactive molecules in vitro and in vivo by means of carbon fiber microelectrodes is now a mature field of research, and has revealed the quantal nature of exocytosis. [1, 2] The research has in particular contributed to a better understanding of neurodegenerative diseases such as Parkinson's and Alzheimer's disease. However, a successful implementation of electrochemistry as a tool in the drug discovery industry relies on the development of suitable automated and parallelized systems. [3] The development of on-chip micro-electrodes for electrochemical sensing is a crucial step to reach this goal. The choice of electrode materials is however challenging, as materials can have very different properties in terms of electrochemistry with different transmitter molecules, signal-to-noise ratios, and potential limits. [4–6] Conducting polymer electrodes of micro patterned poly(3,4-ethylenedioxythiophene) (PEDOT) appear to have excellent properties for neurochemical detection, although the inherent noise is considerably larger than for noble metal and carbon electrodes with same geometry. The noise properties of PEDOT is shown to be attributed to the huge pseudo-capacitance associated with the doping mechanisms involved, where either polystyrene sulfonate or tosylate ions are used as the negative counter ions in the positively charged PEDOT backbone structure. For noble metal and carbon electrodes, only the double layer capacitance contributes to the overall capacitance. However, by exploiting cell adhesion techniques, the response from a large group of neuronal cells can be recorded at PEDOT micro-electrodes, resulting in high signal to noise ratios, and allows for the desired dose-response relationships for added drug compounds to be obtained. [7]

References

[1] Wightman, R. M.; Jankowski, J. A.; Kennedy, R. T.; Kawagoe, K. T.; Schroeder, T. J.; Leszczyszyn, D. J.; Near, J. A.; Diliberto, E. J.; Viveros, O. H. Temporally Resolved Catecholamine Spikes Correspond to Single Vesicle Release from Individual Chromaffin Cells. *Proc. Natl. Acad. Sci. U. S. A.* **1991***, 88*, 10754–10758.

[2] Amatore, C.; Arbault, S.; Guille, M.; Lemaitre, F. Electrochemical Monitoring of Single Cell Secretion: Vesicular Exocytosis and Oxidative Stress. *Chem. Rev.* **2008***, 108*, 2585–2621.

[3] Spegel, C.; Heiskanen, A.; Pedersen, S.; Emneus, J.; Ruzgas, T.; Taboryski, R. Fully Automated Microchip System for the Detection of Quantal Exocytosis from Single and Small Ensembles of Cells. *Lab on a Chip* **2008***, 8*, 323–329.

[4] Larsen, S. T.; Vreeland, R. F.; Heien, M. L.; Taboryski, R. Characterization of Poly(3,4-Ethylenedioxythiophene):Tosylate Conductive Polymer Microelectrodes for Transmitter Detection. *Analyst* **2012***, 137*, 1831–1836.

[5] Larsen, S. T.; Heien, M. L.; Taboryski, R. Amperometric Noise at Thin Film Band Electrodes. *Anal. Chem.* **2012***, 84*, 7744–7749.

[6] Larsen, S. T.; Argyraki, A.; Amato, L.; Tanzi, S.; Keller, S. S.; Rozlosnik, N.; Taboryski, R. Pyrolyzed Photoresist Electrodes for Integration in Microfluidic Chips for Transmitter Detection from Biological Cells. *ECS Electrochem. Lett.* **2013***, 2*, B5–B7.

[7] Larsen, S. T.; Taboryski, R. All Polymer Chip for Amperometric Studies of Transmitter Release from Large Groups of Neuronal Cells. *Analyst* **2012***, 137*, 5057–5061.

16:45 – 17:20

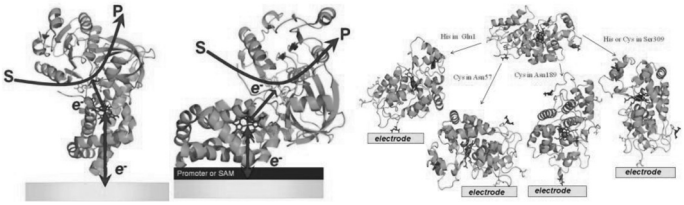
Electronically Wired Proteins: Optimization of Structure-Function Relationships

Elena Ferapontova

Interdisciplinary Nanoscience Center (iNANO) Gustav Wieds Vej 14, Aarhus University, DK-8000 Aarhus C, Denmark
E-mail elena.ferapontova@inano.au.dk

Electrocatalytic and biosensing properties of redox proteins depend on the efficiency of electron transfer (ET) between protein redox centres and electrodes, in particular on ET pathways preconditioned by protein assembly and orientation at electrodes [1]. Here, several strategies for controlled orientation of redox enzymes and proteins are discussed to gain knowledge of their directional ET reactions and ways they can be optimized. Heme- and flavo-containing redox proteins, such as horseradish peroxidase (HRP), containing surface His and Cys tags, bacterial truncated hemoglobin (trHb) and *E. coli* flavohemoglobin (HMP) were coupled to electrodes via genetically introduced surface tags [2], by reconstitution onto heme-terminated SAMs of alkanethiols [3], 3). Covalent attachment via preferentially charged surface aminoacid residues [4] and 3). Adsorbed onto promoter modified electrodes [4]

Attachment of HRP onto electrodes via tags provided its anisotropic orientations, with electrochemically estimated long-range ET rates between the electrode and heme of HRP consistent with theoretically predicted values. In contrast, reconstitution of HRP onto heme-terminated SAM resulted in a low-efficient ET and bioelectrocataysis. Covalent attachment of trHb to functionalized SAMs resulted in ET rates up to 2000 s^{-1} but only for preferential orientations via negatively charge surface domains. More complex HMP, with a Hb-domain fused with an FAD-domain, required a promoter at



the electrode surface to ensure site-specific immobilization of HMP via the heme domain enabling catalysis of reversible NADH/NAD^+ transformation. Comparison of several wiring strategies showed that the highest ET rates and bioelectrocatalysis might be achieved by protein site- and domain-specific immobilizations mimicking the natural environment of the protein and thus providing ET along the most favourable ET pathway within the protein matrix.

References

[1] E. E. Ferapontova, Unmediated enzyme electrodes. in: C. A. Grimes, E. C. Dickey, and M. V. Pishko, (Eds.), Encyclopedia of Sensors, ASP, USA, 2006, pp. 391–422.

[2] A. V. Kartashov, G. Serafini, M. Dong, S. Shipovskov, I. Gazaryan, F. Besenbacher, and E. E. Ferapontova, Phys. Chem. Chem. Phys. 12 (2010) 10098–10107.

[3] M. Sosna, D. Fapyan, E. E. Ferapontova, J. Electroanal. Chem. 728 (2014) 18–25.

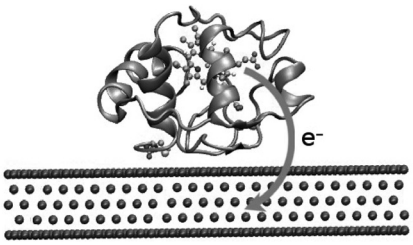
[4] A. Kartashov, D. Fapyan, A. Bonamore A., A. Boffi A., E. E. Ferapontova (2014) in ms.

17:20 – 17:55

Redox active proteins on gold surfaces: insights from a QM/MM approach

Laura Zanetti-Polzi[1,*], Isabella Daidone[2], Carlo A. Bortolotti[1,3] and Stefano Corni[1]

[1)] *Center S3, CNR NANO, Institute of Nanoscience, Via Campi 213/A, 41125, Modena, Italy.*
[2)] *Department of Physical and Chemical Sciences, University of L'Aquila, via Vetoio (Coppito 1), 67010, L'Aquila, Italy.*
[3)] *Department of Life Sciences, University of Modena and Reggio Emilia, Via Campi 183, 41125, Modena, Italy.*
**)E-mail laura.zanettipolzi@nano.cnr.it*



The modeling of redox-active proteins immobilized on solid surfaces has recently received an increasing interest for its importance in several technologically relevant fields such as implementation of bioelectronics, development of biofuel cells and applications in nanotechnology [1, 2, 3].

Despite many potential applications and the fundamental scientific interest, a deep comprehension of the behavior of proteins immobilized on electrodes is still missing. Specifically, electron transfer (ET) processes at the bio-inorganic interface are poorly understood at the microscopic level. An adequate insight into such mechanisms is, however, fundamental for enabling the optimization of the electrical communication between proteins and electrodes, which is a critical issue for the development of biofuel cells. Indeed, although this kind of devices has been since many years the target of intense studies, research on enzymatic biofuel cells is still in the fundamental stage.

When redox-active proteins are studied at electrodes, some fundamental difficulties have to be faced: many proteins undergo denaturation when adsorbed at metal electrodes, resulting in dramatic changes of their ET properties. Even when the functionality is preserved upon surface tethering, the protein orientation towards the surface can severely influence the kinetic

of the ET process. This has led to the suggestion of a number of empirical immobilization strategies aiming at preventing denaturation and facilitating electron exchange within the bioinorganic interface. Yet, central aspects of the problem are thus still unclear and, most notably, appropriate models to study the problem are lacking, confining the development of such systems to trial-and-error approaches. In particular, the use of theoretical and computational methodologies to understand and optimize the behavior of immobilized ET proteins is still in its infancy [2, 4].

A hybrid quantum mechanics/molecular mechanics (QM/MM) approach based on the Perturbed Matrix Method (PMM) is here presented to characterize the thermodynamic properties of the ET reactions of redox proteins immobilized on solid surfaces. Such a method, based on a joint application of MD simulations and QM calculations, provides a reliable modeling of chemical processes in complex molecular systems, preserving both the configurational complexity of the overall atomic-molecular environment and the quantum-chemical description of the chemical event [5, 6]. The PMM approach has been already successfully applied to model several processes (reactions in proteins, the variation of UV and IR spectra as a function of the environment, charge-transfer in solution) and has been recently developed to handle the bio-inorganic interface.

As previously mentioned, the inefficient electron conduction between biocatalysts and electrodes is a critical point in the development of biofuel cells. However, ET reactions are more efficient for those proteins in which at least part of the redox centre is conveniently located at or near the periphery of the protein shell. These proteins are able to carry out direct electron transfer (DET) between the protein active centre and the electrode surface. Obviously, the orientation of the protein on the electrode surface is a key factor affecting the ET activity. Cytochrome c (Cyt c), laccase, hydrogenase and several peroxidases fall into this category.

The study of Cyt c covalently bound to gold is here presented, as it is a benchmark systems of technological relevance. Cyt c is indeed a very well characterized protein that has been extensively studied both experimentally and theoretically and gold surfaces are widely used in several bio-electronics and biological applications. By means of classical molecular dynamics simulations and the Perturbed Matrix Method, the redox potential of Cyt c adsorbed on a bare gold surface is calculated and, after validation by comparison with experimental results, insights are gained on the structural and dynamic determinants to the redox thermodynamics of the adsorbed molecule.

References

[1] I. Willner, Y. -M. Yan, B. Willner, R. Tel-Vered, *Fuel Cells* **1**, 7–24 (2008).
[2] I. Ivanov, T. Vidakovi-Koch, K. Sundmacher, *Energies* **3**, 803–846 (2010).
[3] Y. -S. Chen, M. -Y. Hong, G. S. Huang, *Nat. Nanotechnol.* **7**, 197–203 (2012).
[4] M. H. Osman, A. A. Shah, F. C. Walsh, *Biosensors and Bioelec.* **26**, 3087–3102 (2011).
[5] A. Amadei, F. Marinelli, M. D. Abramo, M. D. Alessandro, M. Anselmi, A. Di Nola, M. Aschi, *J. Chem. Phys.* **122**, 124506 (2005).
[6] A. Amadei, M. D. Alessandro, M. Paci, A. Di Nola, M. Aschi, *J. Phys. Chem. B* **110**, 7538–7544 (2006).

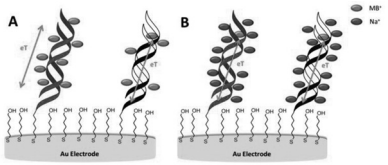
17:55 – 18:20

Electrochemical Analysis of Sequence-Specific Binding of Methylene Blue to Gold-Tethered DNA

Lászlo Kekedy-Nagy[1], Rui Campos[2], and Elena Ferapontova[3,*]

[1),2),3)] *Interdisciplinary Nanoscience Center (iNANO) and Center for DNA Nanotechnology (CDNA) Gustav Wieds Vej 14, Aarhus University, DK-8000 Aarhus C, Denmark*

**)E-mail elena.ferapontova@inano.au.dk*



Electron transfer (ET) in DNA depends on the ET pathways predetermined by interactions of redox active species with DNA molecules [1–3]. Here, interactions between double stranded (ds)DNA tethered to gold electrodes through the alkanethiol linker and the positively charged Methylene Blue (MB) redox indicator capable of intercalating, groove and electrostatic binding to dsDNA were studied at different ionic strengths and MB concentrations (Figure) [4]. The gold surface electrodes were modified with dsDNA composed of G-C 20 base pairs (bp) and A-T 25 bp. Cyclic voltammetry was used for analysis and the ionic strength of the solutions was adjusted by NaCl.

At low MB concentrations the ET between the electrode and G-C DNA-intercalated MB is shown to be mediated by DNA and is characterized by the ET rate constant k_s approaching 40 s^{-1}. Interactions of MB with A-T DNA were restricted solely to the minor and major groove binding; with the apparent DNA-mediated ET rates increased to ca. 70 s^{-1}. This increase was associated with the varying mechanism of the ET reaction and easier protonation of the groove-bound MB as compared to the intercalated MB. At high MB concentrations, MB binding to G-C DNA was no longer restricted to intercalation but also groove and electrostatic binding, which resulted in the higher ET, k_s values approaching those obtained with A-T DNA. By screening the charges, electrostatic interactions and groove binding of MB to DNA were diminished, and the whole ET reaction was governed by diffusion of MB to the electrode surface.

The results show that modes of interaction between MB redox indicator and dsDNA tethered to gold surface electrodes is sequence-specific, and

depend on the concentration of MB and the solution ionic strength.The results are particularly important for understanding the ET properties of DNA and for the development of new concepts of biosensors based DNA-mediated ET reactions.

References

[1] Slinker, J. D.; Muren, N. B.; Renfrew, S. E.; Barton, J. K. *Nature Chem*. 2011, 3, 228–233
[2] Anne, A.; Demaille, C. *J. Am. Chem*. Soc. 2006, 128, 542–557.
[3] Ferapontova E. E., *Curr. Anal. Chem*., 7 2011 51–62.
[4] Kekedy-Nagy, L., Campos, R., Ferapontova, E. **2014**, in preparation.

18:20 – 18:45

Nanostructured metal oxide Li ion battery anode materials: from zero dimension to three dimension

Lin Gao, Xiangru Li, Hao Hu and Ying Yu*

Institute of Nanoscience and Nanotechnology, College of Physical Science and Technology, Central China Normal University, Wuhan 430079, China
**)E-mail yuying01@mail.ccnu.edu.cn*

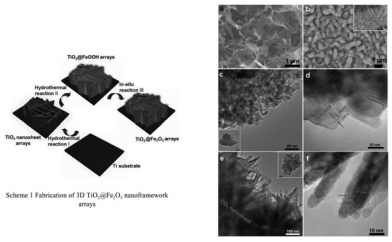


Figure 1 SEM and TEM images of TiO_2 nanosheet arrays and $TiO_2@Fe_2O_3$ arrays

Although graphite is commercially used in Li ion battery anode materials, its specific capacity is too low to meet the requirement for electronic cars. Metal oxides are widely studied to take the place of graphite due to their high capacity performance. However, Li-metal alloying/de-alloying process enlarges the volume change of metal oxide electrode materials for more than 200%, which results in the disintegration of conduction pathways and thereafter poor cyclability and rate performance. In this study, we report that through the tuning the structure from bulk to nanostructure and from zero to three dimensional (3D), the high specific capacity can not lose greatly while cyclability and rate performance can improve substantially [1]. SnO_2 [2] and TiO_2 [3–5] base metal oxides will be demonstrated to show the mechanism of the nanostructure formation and the structure-related performance enhancement. The final conclusion is that the three dimensional structure hybridized with different metal oxides has the best performance. The fabrication process and structure of the demo of 3D $TiO_2@Fe_2O_3$ nanoframework arrays are shown below.

References

[1] J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan, X. W. Lou, *Adv. Mater.* **24**, 5166–5180 (2012).
[2] H. Hu, L. Gao, H. Cheng, J. Liu and Y. Yu, *Nanoscale*. (under revision).

[3] X. Li, H. Hu, S. Huang, G. Yu, L. Gao, H. Liu, Y. Yu, *Electrochim. Acta.* **112,** 356–363 (2013).
[4] L. Gao, X. Li, H. Hu, G. Li, H. Liu, Y. Yu, *Electrochim. Acta.* **120**, 231–239 (2014).
[5] L. Gao, H Hu, G. Li, Q. Zhu, Y. Yu, *Nanoscale.* **6**, 6463–6467 (2014).

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