Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Focus Topic
Room: 317 - Session QC+AS+BI+MN-ThM

Fundamentals and Method Development of QCM
Moderator: Ralf Richter, CIC biomaGUNE & MPI for Intelligent Systems, W.K. Hiebert, University of Alberta and The National Institute for Nanotechnology

8:40am **QC+AS+BI+MN-ThM3 High-Frequency Contact Mechanics Studies with a QCM**, ***Diethelm Johannsmann***, Clausthal University of Technology, Germany **INVITED**

Studying particulate objects with a QCM is challenging with regard to interpretation, but also of outstanding interest. Potential samples would be (bio-) colloids, vesicles, granular matter, bacteria or technical multi-contact interfaces. The analysis must build on the small-load approximation, which states that the shifts in resonance frequency and resonance bandwidth are proportional to the in-phase and the out-of-phase component of the area-averaged stress at resonator surface. For realistic modeling, a numerical code is needed which predicts this stress field from the geometry and all materials parameters involved. There is such a model in two dimensions, building the finite element method.

On a simpler level, the behavior of particles on a resonator surface can also be understood from the coupled resonance model. The particles in contact form small resonators of their own, where the "particle resonance frequency" is determined by the mass and the stiffness of the contact. If the particle resonance frequency in the range of frequencies amenable to the QCM one observes a coupled resonance, meaning that the shifts of resonance frequency and resonance bandwidth themselves form a resonance curve when plotted versus overtone order. Depending on whether the particle resonance frequency is higher or lower than the QCM frequency, the frequency shift can be positive or negative. From the particle resonance frequency, one can assess the stiffness of the contact between the particle and the surface.

The detailed investigation of the coupled resonance picture reveals a problem. though. FEM models of the corresponding geometries reveal two coupled resonance, occurring at different frequencies. They corresponding to a rotation of the particle about the point of contact (the "rocking mode") and a rotation about the center of mass (the rotational mode"). The problem complicates the interpretation of experimental data, but it points to an intriguing analogy between QCM experiments a vibrational spectroscopy. A QCM experiment amounts to a vibrational spectroscopy on surface-attached colloids.

The last part of the talk is concerned with a novel sensing dimension of the QCM, which is the dependence of frequency and bandwidth on amplitude. Such dependences are ubiquitous in contact mechanics experiments and can be understood in terms of partial slip. The contacts behave nonlinearly. Nonlinear behavior can also be observed in liquids, where it is caused by the nonlinear term in the Navier-Stokes equation. The nonlinear term drives a steady flow of liquid along the direction of oscillation towards the center of the plate.

9:20am **QC+AS+BI+MN-ThM5 Study of Water Adsorption and Capillary Bridge Formation for SiO_2 Nanoparticle Layers by Means of a Combined *In Situ* FT-IR Reflection Spectroscopy – QCM-D Set-up**, ***Boray Torun***, *C. Kunze,* University of Paderborn, Germany, *C. Zhang, T.D. Kühne,* Johannes Gutenberg University Mainz, Germany, *G. Grundmeier*, University of Paderborn, Germany

During the past decade nanoparticles attracted a great deal of attention and found many applications in various fields ranging from pigments and antibacterial agents to highly effective catalysts. In this context, the handling and processing of nanoparticle powders play an important role. In contrast to macroscopic particles, nanoparticle flow properties are manly governed by the particle-particle interactions. The forces determining these interactions strongly vary not only with the material properties but also with surface chemical composition as well as the environmental conditions. Hence, a fundamental understanding of the processes and forces involved plays a key role for the prediction of nanoparticle powder behavior.

In the presented study [1], water adsorption and capillary bridge formation within a defined layer of SiO_2 nanoparticles was studied by means of a novel *in-situ* analytical setup allowing for combined quartz crystal microbalance with dissipation analysis (QCM-D) and Fourier transformation infrared reflection absorption spectroscopy (FT-IRRAS). On the one hand, the QCM-D gave insights on both, mass change (Δf) and changes in the contact mechanics, indicated by dissipation changes ($\Delta\Gamma$), whereas on the other hand FT-IRRAS allowed for the characterization of the adsorbed water structure. Employing peak deconvolution to the OH-signal in the region of 3400 cm^{-1}, "ice-like" and "liquid-like" water structures could be clearly identified.

Combined measurements show that for a monolayer of monodisperse SiO_2 particles with a diameter of about 250 nm the adsorption of water leads to a linear increase in dissipation for relative humidity (RH) values up to 60%. Subsequently, the strong increase in dissipation between 60% and 80% RH was attributed to the actual liquid bridge formation. This result was supported by the predominant growth of "liquid-like" water during the bridge formation phase indicated by the corresponding FT-IR data. Furthermore, for RH>90% a decrease in dissipation was detected indicating the merging of capillaries and the onset of a water film formation. Overall, our results indicate that combined in-situ QCM-D and FT-IRRAS analysis enables the qualitative and quantitative analysis of water adsorption and capillary bridge formation in particle layers.

[1] Torun, B. et al., *Phys. Chem. Chem. Phys.*, **2014**, 16, 7377-7384

9:40am **QC+AS+BI+MN-ThM6 On the Role of Acoustic Streaming in Particle Detachment Events at a QCM Surface**, ***Rebekka König***, *A. Langhoff, D. Johannsmann*, Clausthal University of Technology, Germany

A steady flow of liquid was observed above the surface of a quartz crystal microbalance (QCM) under conditions, where the oscillation amplitude exceeded 10 nanometers . The streaming flow occurs parallel to the displacement vector and is directed towards the center of the plate. It is expected to have applications in acoustic sensing, in microfluidics, and in micromechanics in a wider sense. The flow is caused by the nonlinear term in the Navier- Stokes equation, which can produce a nonzero time-averaged force from a periodic velocity field. Central to the explanation are the flexural admixtures to the resonator's mode of vibration. Unlike pressure-driven flows, the acoustically driven steady flow attains its maximum velocity at a distance of a few hundred nanometers from the surface. It is therefore efficient in breaking bonds between adsorbed particles and the resonator surface. As a side aspect, the flow pattern amounts to a diagnostic tool, which gives access to the pattern of vibration. In particular, it leads to an estimate of the magnitude of the flexural admixtures to the thickness-shear vibration.

[1] R. König, A. Langhoff, D. Johannsmann, *Physical Review E***2014**.

11:00am **QC+AS+BI+MN-ThM10 QCM for Particle Sizing and Beyond**, ***Adam Olsson***, *I.R. Quevedo, D. He, M. Basnet, W. Lee, N. Tufenkji*, McGill University, Canada **INVITED**

The dissipative energy loss of a quartz crystal microbalance (QCM) sensor is typically ascribed to the viscoelastic nature of the adsorbed material. While such an interpretation is suitable for thin homogeneous films, it is not *a priori* valid for discrete objects. As demonstrated recently, dissipation due to nanoparticle deposition can be described by the relative movement of the particles attached to the oscillating sensor surface. This particular dissipation behavior of nanoparticles gives rise to new experimental approaches to study colloidal transport, particle-surface interactions and particle properties.

In this presentation, we focus on QCM-D as a method to determine the size of deposited nanoparticles. The approach involves analysis of the change in dissipation per attached mass (i.e., the "$\Delta D/\Delta f$-ratio") to predict a hypothetical full particle surface coverage that can be used to calculate an effective layer thickness of the particulate film; and this quantity, in turn, can be related to the average particle diameter. To validate the approach, we determined particle sizes using various types of nanoparticles with diameters ranging from ~ 5 nm to ~ 110 nm and compared the results with sizes obtained from dynamic light scattering (DLS) and transmission electron microscopy (TEM). We found that accurate particle sizing is possible, but requires firm coupling between the particle and the sensor surface. Hence, if the particle size is known, the approach can also be used to investigate the strength of the nanoparticle-surface interaction.

We will also describe our ongoing work where we are studying the QCM-D response to the deposition of anisotropic bacteriophage to determine their orientation on the surface. Bacteriophages are viruses that bind to and infect bacteria with high specificity and, thus, can be exploited in antimicrobial and biosensor applications. One challenge in functionalizing surfaces with bacteriophages is to control their orientation such that their binding sites remain exposed to the ambient medium. By studying how dissipation changes with phage surface coverage, it is possible to identify at which surface coverage phage-phage interaction occurs. This event compromises

the phages ability to bind to bacteria, as evidenced by subsequent bacterial "capture" experiments and imaging, and thus is crucial for the performance of QCM-D based biosensors that utilize bacteriophage as a biorecognition element.

11:40am **QC+AS+BI+MN-ThM12 Full Experimental Proof of the Relationship between the Intrinsic Viscosity of DNA and the Acoustic Ratio of SAW and TSM Sensors**, ***Achilleas Tsortos***, IMBB-FORTH, Greece, *G. Papadakis,* NCSR-Demokritos, Greece, *E. Gizeli*, IMBB-FORTH & Univ. of Crete, Greece

Acoustic wave sensors are extensively used in biotechnology and biophysics in order, for example, to detect molecules in a solution, study an antibody-antigen interaction or the hybridization of DNA. Today, data analysis includes (a) the use of the Sauerbrey equation, in order to calculate the mass of the molecules attached on the surface of the acoustic device by use of frequency data and (b) the use of complicated mathematical models of the assumed 'film' formed by the attached molecules. In the second case information such as the rigidity modulus and viscosity of the 'film' can be calculated and comments can be made on the softness (viscoelasticity) of the added layer.

Here, we present an entirely different approach. Based on a theory developed earlier[1,2] we correlate the acoustic ratio R, to the intrinsic viscosity $[\eta]$ of the attached molecule. The acoustic ratio is the ratio of the amount of energy loss per attached unit mass – this is given as $(\Delta D/\Delta F)$ in the TSM acoustic mode notification, or as $(\Delta A/\Delta Ph)$ in the SH-SAW mode and is readily obtained in each experiment. The *intrinsic* viscosity on the other hand, is a hydrodynamic quantity directly related to the size and shape of a biomolecule and can be determined independently through viscometry. In this study we present collected experimental data from a variety of case studies proving for the first time the semi-empirically assumed relationship $R\sim[\eta]$ in a general form. Data are presented for various shapes and sizes of DNA and other systems of biological interest. The case is made for two acoustic modes (thickness shear and surface horizontal) and for various frequencies in the range of 5-155 MHz.

Our analysis presents a paradigm shift and challenge; we claim that (label-free) structure probing is a much more improved method offering higher flexibility in design and interpretation of experimental assays. Detecting and monitoring in real time processes that involve structural changes but not necessarily mass changes and/or 'film' formation is a novel concept that can be readily applied in anything from DNA, RNA hybridization and detection of mutations to molecular machines (e.g. DNA Holliday junction) and protein/DNA/RNA interactions in the broad areas of biophysics, s tructural DNA nanotechnology and diagnostics.

Acknowledgement: the REGPOT-InnovCrete/EU-FP7 (Contract No. 316223) for financial support.

References:

1. A. Tsortos, et al., *Biophys. J.* 2008, 94:2706

2. A. Tsortos, et al., *Biosens. Bioelectron.* 2008, 24:836

12:00pm **QC+AS+BI+MN-ThM13 Characterization of the Conformation of Linker-Suspended Proteins at Surfaces through Acoustic Ratio Measurements**, ***Electra Gizeli***, IMBB-FORTH & Univ. of Crete, Greece, *D. Milioni,* IMBB-FORTH, Greece, *G. Papadakis,* NCSR-Demokritos, Greece, *A. Tsortos*, IMBB-FORTH, Greece

Characterization of protein shape and orientation following surface binding is an area of great interest in biophysics with many applications in chemistry and nano/biotechnology. Techniques such as ellipsometry and AFM have been extensively used for providing such information. A lot of effort has also been put with acoustic sensors; results in this case though depend greatly on the data interpretation model employed. An important question is always the preservation of protein integrity/form.

In this work we employ acoustic devices based on a QCM geometry at 35 MHz. The acoustic ratio $\Delta D/\Delta F$, i.e., the dissipation over frequency change of the shear wave has been employed in our analysis. We have previously shown[1] that as a tool, this ratio provides valuable information regarding the conformation of surface attached DNA molecules; we have also employed this approach in the design of DNA assays for diagnostic purposes, including detection of sequence targets in real samples[2].

Here we expand this methodology in proteins; streptavidin is used as a case study for characterizing spherical protein immobilization on an acoustic device. Good control of the binding mode was achieved by changing the distance of the protein from the surface, ranging from zero (direct physisorption) to several nm, using anchor molecules. In this way we can manipulate the degree of surface interference to the protein structure. Our results clearly show that direct protein adsorption is a multistep process resulting in very low acoustic ratio, in agreement with the literature. However, we show for the first time that suspending the protein away from the surface from a single point through a variable-length linker, gives an entirely different picture; the process is a single-step event, as judged from D-F plots, and the resulting acoustic ratio is much higher (order of magnitude) than that obtained in physisorption. The effect of the linker length on the apparent acoustic ratio is analyzed. This approach gives more reliable and different information regarding the protein shape than do simple physisorption protocols and interpretation models involving notions such as 'film' formation etc.

References:

1. A. Tsortos, et al., *Biosens. Bioelectron.* 2008, 24:836; A. Tsortos et al., *Biophys. J.* 2008, 94:2706

G. Papadakis et al., *Anal. Chem.* 2012, 84:1854; G. Papadakis et al., *Scientific Rep.* 2013, 3:2033

Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Focus Topic
Room: 317 - Session QC+AS+BI+MN-ThA

Applications of QCM

Moderator: Electra Gizeli, IMBB-FORTH, Heraklion, Crete,Greece, Adam Olsson, McGill University, Canada

2:20pm **QC+AS+BI+MN-ThA1 Permeability of a Model Stratum Corneum Lipid Membrane**, ***Daeyeon Lee***, University of Pennsylvania **INVITED**

The stratum corneum (SC), composed of corneocytes and intercellular lipid membranes, is the outermost layer of the epidermis, and its main function is the regulation of water loss from the skin. The major components of the SC lipid membranes are ceramides (CER), cholesterol (CHOL), and free fatty acids (FFA), which are organized in multilamellar structures between corneocytes. The intercellular SC lipid membrane is believed to provide the main pathway for the transport of water and other substances through the skin. While changes in the composition of the SC lipid membranes due to intrinsic and/or extrinsic factors have been shown to affect the organization of the lipid molecules, little is known about the effect of compositional changes on their water permeability. In this talk, I will present our results on the effect of composition on the permeability of a model SC lipid membrane consisting of ceramide, palmitic acid, and cholesterol using a quartz crystal microbalance with dissipation monitoring (QCM-D). The QCM-D method enables the direct determination of the diffusivity (D), solubility (S), and permeability (P) of water through the model SC lipid membranes. In the first part, I will discuss the effect of membrane composition on the water permeability of the model SC lipid membrane. We find that D and S weakly depend on the chain length of saturated fatty acids, while P shows no significant dependence. In contrast, the saturation level of free fatty acids and the structure of ceramide have significant influence on D and S, respectively, resulting in significant changes in P. In the second part of the talk, I will present our recent work on the effect of common anionic surfactants on the water permeability of the model SC lipid membrane. Particularly, the effect of sodium dodecyl sulfate (SDS) and sodium lauryl ether sulfate (SLES) with one or three ethoxy groups on the water permeability of the model SC lipid membrane is compared.

3:00pm **QC+AS+BI+MN-ThA3 Investigation of Interaction between a Monoclonal Antibody and Solid Surfaces via Multiple Surface Analytical Techniques**, ***Xia Dong***, *C.A.J. Kemp, Z. Xiao*, Eli Lilly and Company

The interaction between proteins and surfaces is an important topic in the field of biomaterials. With the development of monoclonal antibody products, there is increasing interest in understanding the nature of the interactions between antibodies and the solid surfaces they contact during manufacturing processes and storage. In this study, a monoclonal antibody was introduced to quartz crystal microbalance (QCM) substrates coated with gold, stainless steel and silicon carbide. The samples were characterized by multiple surface analytical techniques, including TOF-SIMS and XPS. The preliminary XPS results suggest that the protein adsorbed at higher concentration on gold than on stainless steel and silicon carbide, while nitrogen concentration detected on stainless steel is slightly higher than on silicon carbide. This is generally consistent with the QCM results. TOF-SIMS spectra also suggest that the interaction between the antibody and three substrates is not the same. The fragmentation patterns detected in the TOF-SIMS spectra obtained from silicon carbide and stainless steel are similar to each other, but they are different from those detected on gold. The interaction between the antibody and stainless steel coupons will be further studied to understand the influence of surface morphology.

3:20pm **QC+AS+BI+MN-ThA4 Combining Spectroscopic Ellipsometry and Quartz Crystal Microbalance to Study Biological Hydrogels – Towards Understanding Nucleo-Cytoplasmic Transport**, *N.B. Eisele, S. Ehret, R. Zahn,* CIC biomaGUNE, Spain, *S. Frey, D. Gorlich,* MPI Biophysical Chemistry, Germany, ***Ralf Richter***, CIC biomaGUNE & Université Grenoble Alpes & MPI Intelligent Systems, Spain

Nature has evolved hydrogel-like materials that are exquisitely designed to perform specific biological functions. An example of such a material is the nuclear pore permeability barrier, a nano-sized meshwork of intrinsically disordered proteins (so called FG nups) that fills the nuclear pores (i.e. the roughly 40 nm wide channels across the nuclear envelope) and controls the entry of macromolecules into the nucleus of eukaryotic cells. The permeability barrier exhibits a unique selectivity in transport: very small molecules can cross the barrier efficiently, while larger objects are delayed or blocked unless they are bound to specialized proteins, so called nuclear transport receptors (NTRs). How size and species selectivity are encoded in the hydrogel-like properties of the permeability barrier is currently not well understood.

We have developed monolayers of end-grafted FG nups as a nano-scale model system of the permeability barrier. The planar geometry of this well-defined biomimetic film affords detailed and quantitative characterization – not accessible for the native system - with a toolbox of surface-sensitive characterization techniques. In particular, we present the application of the *in situ* combination of quartz crystal microbalance (QCM-D) and spectroscopic ellipsometry (SE) to quantify film thickness, hydration and viscoelastic properties as a function of protein surface density.

We will present how this experimental data, combined with polymer theory, allows us to better understand the relationship between the supramolecular organization and dynamics of the permeability barrier, its physico-chemical properties and its biological function. We demonstrate that attractive interactions between FG nups play an important role in tuning the assembly and morphology of FG nup meshworks, and highlight that even rather weak interactions – typically a few *kT* per biopolymer chain – have functional importance. We show also how the interaction between NTRs and FG nup meshworks is tuned to afford strong enrichment and at the same time rapid entry and exit of NTRs in the permeability barrier, thereby facilitating NTR translocation.

Taken together, these studies contribute important information to understand the mechanism of size-and species-selective transport across the nuclear pore permeability barrier. The mechanistic insight gained should be useful towards the design of bioinspired species-selective filtering devices. Moreover, the presented procedures for the acquisition and analysis of combined QCM-D/SE data are broadly applicable for the characterization of ultrathin biomolecular and other polymer films.

4:00pm **QC+AS+BI+MN-ThA6 Probing Nanoparticle-Biofilm Interactions using Quartz Crystal Microgravimetry and Complementary Surface-sensitive Methods**, ***Kaoru Ikuma****, University of Massachusetts, *Z. Shi, A.V. Walker,* University of Texas at Dallas, *B.L.T. Lau*, University of Massachusetts

The environmental fate and transport of nanoparticles (NPs) have been a rising topic of concern due to the increased use of nanotechnology. Recent studies have shown that NPs are likely to interact readily with and accumulate in environmental biofilms. Biofilms are a ubiquitous form of microbial presence where cells attached on solid surfaces are surrounded by a sticky matrix of extracellular polymeric substances (EPS). The EPS matrix is considered to be highly heterogeneous and chemically complex. Polysaccharides and proteins are known to be major constituents of EPS and may greatly impact the likelihood of interactions occurring between NPs and biofilms.

In this study, we examined the deposition of NPs onto surface-immobilized proteins to determine the importance of protein-rich domains in the interfacial interactions between NPs and biofilms. Such interfacial processes are the initial and potentially rate-limiting step in NP-biofilm interactions. The deposition kinetics and extent of model hematite (α-Fe_2O_3) NPs onto protein-coated silica surfaces were quantitatively measured by quartz crystal microbalance with dissipation (QCM-D). Model proteins including bovine serum albumin (BSA) and lysozyme as well as bacterial total proteins were used herein. The proteins were initially adsorbed onto either negatively-charged bare or positively-charged poly-L-lysine (PLL)-precoated silica sensors to assess the effects of the orientation of surface-immobilized proteins. In addition to QCM-D, other complementary surface-sensitive techniques such as Kelvin probe force microscopy and time-of-flight secondary ion mass spectrometry (TOF SIMS) were used to characterize the mechanisms of interaction between the NPs and the protein-coated surfaces.

QCM-D results indicated that for all tested proteins, the total deposition extent of hematite NPs was significantly greater on protein layers that were adsorbed onto bare silica compared to PLL-precoated silica sensors. TOF SIMS results showed that the amino acid profiles of the topmost surface of the protein layers on bare and PLL-precoated silica sensors were distinctly different, suggesting that NP deposition was greatly influenced by the

---

*** QCM Focus Topic Young Investigator Award**

orientation of the surface-immobilized proteins. Both the extents and rates of NP deposition were also dependent on the type of model protein. Based on the surface charge, topography, and hydrophobicity characterization results, the observed interfacial interactions between hematite NPs and surface-immobilized proteins appeared not to be controlled by one dominant interaction force but by a combination of electrostatic, steric, hydrophobic, and other interactions.

4:20pm **QC+AS+BI+MN-ThA7 Association and Entrapment of Membrane-Targeted Nanoparticles with Different Binding Avidity: A QCM-D and sIngle Particle Tracking Study**, ***Anders Lundgren****, *B. Agnarsson, S. Block, F. Höök*, Chalmers University of Technology, Sweden

Nanoparticles specifically targeted to receptors in the cell membrane are interesting for various applications such as intracellular delivery and visualization of diffusing membrane proteins, so-called single particle tracking. These diverse applications require particles optimized to display different binding properties: In this model study we investigated the effect of particle size and ligand density on the association rate and mobility/entrapment of biotin functionalized core-shell nanoparticles to supported lipid bilayers sparsely modified with streptavidin. Gold-PEG core-shell nanoparticles were synthesized with two different core sizes, 20 and 50 nm in diameter, and a shell (10 nm) of mixed uncharged, negatively charged and biotinylated PEG-ligands, the biotin content varied from one to several hundreds per particle. Particle binding was examined on the ensemble level using QCM-D and on single particle level using novel light scattering microscopy that will be detailed. At physiological salt conditions, binding of 50 nm particles were weakly dependent on the number of displayed biotin ligands, whereas the association of 20 nm particles were strongly attenuated in direct relation to the ligand density. At low salt conditions, binding of the larger particles resembled that of the smaller particles, with a strong dependence on ligand density. PEGylated particles without biotin-ligands did not bind at any condition. Thus, it was concluded that specific particle affinity is strongly attenuated by particle size and surface charge due to different interaction potential between the particle and the surface. On the contrary, no dependence on particle size was observed for the mobility of single particles displaying diffusion constants close to 0.4 or 0.8 $\mu m^2/s$ irrespective of particle size, which was similar to ensemble measurements using FRAP data on FITC-labelled streptavidin (0.5 $\mu m^2/s$). Only particles with a single surface tether show continuous diffusion; after formation of a second surface bond particles got quickly entrapped and formed additional bonds. In QCM-D measurements, this was manifested by a continuously decreasing dissipative response per particle for binding of particles with increasing ligand density. Together, QCM-D and particle tracking data indicates that two different mechanisms may lead to particle trapping and ultimately particle wrapping: For very high ligand densities membrane receptors in the membrane diffuse to and partly wraps around immobile particles, whereas for intermediate ligand densities the diffusion and dynamics of the particles themself facilitate the formation of additional surface bonds and eventual wrapping.

4:40pm **QC+AS+BI+MN-ThA8 Complementary Chemiresistor and QCM Studies of Biomacromolecules as Sorptive Materials for Vapor Sensing**, ***Kan Fu***, *X. Jiang, B.G. Willis*, University of Connecticut

Biomolecules are integral components of current sensing and diagnostic technologies including enzymatic glucose sensors, DNA microarrays, and antigen-antibody assays. The use of biomolecules in non-biological situations, however, is a burgeoning new field that may break the existing boundaries of biomolecule applications in exclusively biological context. Extensive studies have already been performed in bioelectronics using small biomolecules and biomacromolecules, revealing promising results regarding charge transport and conformation dependence. In the area of sorptive chemical sensors, biomacromolecules have inherent advantages over conventional synthetic polymers. DNA oligomers have precisely defined sequences through synthesis, they are monodisperse, and they can self-assemble into nanoscale structures. These features make them interesting for vapor sensing of small molecules.

In this work, a series of 8 custom-designed, single-strand DNA (ssDNA) were integrated with chemiresistors and QCM to make sensors. Chemiresistor sensors were made by depositing gold nanoparticles functionalized with ssDNA molecules onto microfabricated electrodes, and QCM sensors were made by depositing films of ssDNA on quartz crystals. While chemiresistors give high signal-to-noise ratios and significantly better limits of detection (LODs) and may eventually be the transducer for practical applications, QCM is a purely mass-sensitive technique that reveals fundamental absorption properties in terms of partition coefficients. By exposing these sensors to a series of organic vapors, the resistance change and mass change of the two sensor platforms can be compared. It is demonstrated that, similar to previous comparative studies of gold nanoparticles functionalized with small organic thiols and synthetic polymer modified QCM crystals, the nanoparticle-based chemiresistor response follows the QCM-traced mass change. The studies show that sorption and conductance modulation mechanisms of vapors on biomolecules are similar to sensors with small organic molecules, but the polarity preference is very different. A model relating partition coefficients K in and chemiresistor responses $\Delta R/R$ is thereafter suggested to account for the links between these 2 sensing systems. It needs to be noted that points which deviate from the modeled trends are likely the result of more complex vapor-material interactions. From here, we demonstrate that DNA oligomers are rich in diversity, which may qualify these materials for array-based and specific sensing applications. It also establishes QCM as a useful complementary tool for evaluating materials for various sensing systems.

5:00pm **QC+AS+BI+MN-ThA9 The Evolution of Complex Artificial Cell Membranes: Combining Patterned Plasma Polymers and Supported Lipid Bilayers**, ***Hannah Askew***, *S.L. McArthur*, Swinburne University of Technology, Australia

Supported lipid bilayers (SLBs) have provided researchers with stable and reproducible platforms to recreate cell membrane environments. Such models are useful for studying a variety of processes including cell signalling and drug-membrane interactions. Unfortunately, current models are lacking in their ability to mimic complex micro and nanoscale architectures found within native cell membranes. Many methods of SLB patterning have emerged to form these complex structures. In particular pre-patterned substrates combined with vesicle collapse are of great interest as they eliminate complications associated with preserving membrane integrity during patterning. Plasma polymerisation provides a versatile, one step, dry method of creating thin films of different chemistries on almost any substrate. Successful bilayer formation on such coatings would be beneficial for promoting specific organisation in complex SLB systems using patterned surface chemistries. In the initial stages of this work we studied the effect of plasma polymer chemistry on the lipid structures formed using vesicle collapse. DOPC lipid vesicles were introduced to commonly used coatings formed from plasma polymerised allylamine (ppAAm) and acrylic acid (ppAAc). The coatings were characterised using X-Ray Photoelectron Spectroscopy (XPS), contact angle and Quartz Crystal Microbalance with Dissipation (QCM-D) techniques. Lipid interaction kinetics and lipid mobility were characterised using QCM-D and Fluorescence Recovery after Photobleaching (FRAP) respectively. It was shown that a variety of lipid structures including mobile bilayer can be formed on ppAAc using pH alone to control electrostatic interactions. ppAAm formed immobile vesicular layers under all conditions tested and could therefore be used as a barrier to confine fluid areas of bilayer. Work is now being undertaken to create single and dual plasma polymer patterns on both glass and silicon wafer. Standard photolithography and ion beam methods will be employed to pattern on both a micro and nanoscale. In this way plasma polymer patterns may enable the formation of increasingly complex SLB architectures.

5:20pm **QC+AS+BI+MN-ThA10 Applications of QCM in Industrial R&D**, ***Andrey Soukhojak***, The Dow Chemical Company

An overview of diverse applications of QCM enabled by its unparalleled sensitivity to mass and viscoelastic properties of thin samples in R&D of The Dow Chemical Company will be presented.

*** QCM Focus Topic Young Investigator Award**

Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Focus Topic
Room: Hall D - Session QC+AS+BI+MN-ThP

Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Poster Session

QC+AS+BI+MN-ThP1 *In Situ* Toxic Nano-Material Sensing Method Using DNA Immobilized Quartz Crystal Microbalance, ***Kuewhan Jang***, *S. Lee, J. You, C. Park, J. Park, S. Na*, Korea University, Republic of Korea

Nano-material has grown from scientific interest to commercial products and there are more than 1600 nano-material products on the market. Among those nano-materials, single-walled carbon nanotube (SWNT) and silver ion have been shown great interest due to their extraordinary properties. Since SWNT and silver ion production capacity increases each year, its contamination to the environment water system will increase in the form of industrial waste. Moreover, toxicity assessment of those materials is required for human health and environmental issue since the toxicity of those materials has been reported. In this study, we propose the in-situ detection of SWNT and silver ion. The detection mechanism is based on the measurement of the resonance frequency shift arisen from the binding on the DNA immobilized quartz crystal microbalance. We are able to detect SWNT and silver ion less than an hour with the detection limit of 100 ng/ml of SWNT and 100 pM of silver ion, respectively. Moreover, the DNA immobilized quartz crystal microbalance enables the detection in real tap water. This work shows the potential of DNA immobilized quartz crystal microbalance as the in-situ toxic nano-material screening tool.

QC+AS+BI+MN-ThP2 Mechanics of Multicontact Interfaces Studied with a QCM, *R. König, S. Hanke, J. Vlachová, D. Johannsmann,* ***Arne Langhoff***, Clausthal University of Technology, Germany

The contact stiffness and the contact strength at interfaces between rough surfaces are of outstanding relevance in many different fields, including mechanical engineering, bio-lubrication, and technical tribology.

Individual sphere-plate contacts have been previously investigated with a QCM and it was found that the contact stiffness can be inferred from the frequency shift, where the latter is positive because contact increases the overall stiffness of the composite resonator. At elevated amplitude of oscillation, the apparent contact stiffness decreases because of partial slip. Partial slip (also: “microslip”) describes the situation, where a contact partly sticks and partly slips. Sticking mostly is observed in the center. Slip is found at the edges, where the local stress is large.

The presentation describes the extension of this work to multicontact interfaces as well as the new results which were found with the single contacts . Generally speaking, multicontact interfaces differ from individual contacts by, firstly, a broad distribution of contact size and contact strength and, secondly, by an elastic coupling between neighboring load-bearing asperities.

Different materials (aluminum, PMMA) and different characteristic scales of roughness (all in the range of many microns) were studied. The focus is on polymer surfaces, which where treated with an abrasive paper. A novel geometry, where the resonator is symmetrically loaded with the same type of sample from both sides, has allowed to increase the normal force by a factor of 10, compared to previous experiments.

At small amplitudes, the frequency response of the QCM to a contact with rough PMMA surfaces is similar to the behavior observed with individual sphere-plate contacts. There is an increase in resonance frequency, which can be converted to an interfacial stiffness. Interesting, the contact stiffness observed with MHz excitation was found to much higher than what has been found similar samples with excitation frequencies in the kHz range.

At elevated amplitudes, the behavior is variable. Often one finds partial slip. Occasionally, however, there is a sharp increase in contact stiffness at a certain threshold in amplitude. The bandwidth goes through a maximum at that same amplitude. The behavior is reversible; the threshold is the same for decreasing and increasing amplitude ramps. We tentatively associate the increased apparent stiffness with an oscillation-induced increase in contact area.

[1] S. Hanke, J. Petri, D. Johannsmann, *Phys. Rev. E* **2013**, *88*.

[2] P. Berthoud, T. Baumberger, Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences **1998**, 454, 1615–1634.

Authors Index

Bold page numbers indicate the presenter