

Monday Afternoon, October 19, 2015

Nanometer-scale Science and Technology
Room: 212B - Session NS+AS+SP-MoA

Optical Spectroscopy at the Nanoscale

Moderator: Craig Prater, Anasys Instruments

2:20pm **NS+AS+SP-MoA1 Nanoscale Infrared Spectroscopy Characterization of Amyloid Aggregates Structure**, *Francesco Simone Ruggeri*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *T. Muller*, University of Cambridge, UK, *D. Galante*, CNR, Italy, *T.P.J. Knowles*, University of Cambridge, UK, *H. Lashuel*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *C. D'Arrigo*, CNR, Italy, *G. Dietler*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland
INVITED

Aging of world population has increased the onset of several neurodegenerative disorders (ND). These diseases are connected with insoluble fibrillar proteins aggregates, termed Amyloid. During their aggregation, starting monomeric proteins undergo internal structural rearrangement bringing to fibrils with a final universal cross β -sheet quaternary structure. This structure is independent by the monomeric initial one and it is the fingerprint of amyloid and related diseases. Previously, the final fibrillar cross- β sheet structures were considered the cause of the illnesses. Nowadays, there is strong evidence that the intermediate oligomeric stages of fibrillation could be the cytotoxic one and most of the research groups are investigating the early stages of fibrillation and the inter-conversion of monomers into fibrils. Infrared spectroscopy is a key method for studying conformational properties of proteins and their structural conversion during amyloid fibrillation. Unfortunately, this and others bulk techniques are just able to give average information of the heterogeneous aggregating amyloid solution. To study the chemical structure of amyloid species at the nanoscale, we utilized a thermomechanical detection technique based on atomic force microscopy (nanoIR). If an IR pulse is absorbed by a sample, the local temperature rises and leads to a local thermal expansion. This deformation excites mechanical resonances of the AFM cantilever, in contact with the sample, allowing simultaneously acquiring topography, nanoscale chemical IR maps and/or spectra. We focused on the study of different amyloidogenic proteins, as α -synuclein, lysozyme and $\alpha\beta$ 2. We measured chemical spectra and IR maps of monomeric and fibrillar aggregates. For the first time, we distinguished chemically different amyloid structures at the single aggregate nanometer scale. Nanoscale chemical characterization of amyloidogenic structures as oligomers, protofibrils and fibrils is central to understand how proteins misfold and aggregate, to unravel the structural rearrangement of monomers inside amyloid fibrils and to target pharmacological approach to ND.

3:00pm **NS+AS+SP-MoA3 Recent Progress in Tip-Enhanced Mid-Infrared Photoexpansion Nanospectroscopy**, *M. Jin, F. Lu, Mikhail Belkin*, The University of Texas at Austin
INVITED

Mid-infrared absorption spectroscopy in the molecular fingerprint region ($1/\lambda \sim 600\text{--}4000\text{ cm}^{-1}$) is widely used for chemical identification and quantitative analysis. The ability to perform mid-infrared spectroscopy with nanometer spatial resolution is highly desired for applications in chemical, materials, and life sciences. Nanoscale mid-infrared spectra can be obtained by detecting mechanical forces exerted by sample on an atomic force microscope (AFM) tip upon sample light absorption and photoexpansion. The first demonstration that photoexpansion of bulk polymers can be detected by AFM and used for mid-infrared nanospectroscopy was by Alexander Dazzi and co-workers [1]. However, only relatively thick polymer samples (approximately 50-nm-thick or thicker) produced detectable cantilever deflections in these experiments, even when mid-infrared optical intensity was close to sample damage. We demonstrated that the sensitivity of mid-infrared photoexpansion nanospectroscopy, also known as AFM-IR, may be improved by several orders of magnitude if we send low-power laser pulses at a repetition frequency that is tuned in resonance with the mechanical vibrational frequency of an AFM cantilever and if we further employ tip-enhancement of the optical field below a sharp gold-coated AFM tip. As a result, monolayer sensitivity and 25 nanometer spatial resolution was achieved for molecular imaging in air [2]. We will discuss details of these experiments and recent progress of this technique, including development of background suppression methods that may lead to further enhancement in sensitivity and progress towards achieving photoexpansion nanospectroscopy of samples in aqueous environment that requires mitigation of liquid damping of cantilever vibration and strong infrared absorption.

[1] A. Dazzi, R. Prazeres, F. Glotin and J.M. Ortega, Opt. Lett. 30, 2388 (2005).

[2] F. Lu, M. Jin and M.A. Belkin, Nature Photonics 8, 307 (2014).

3:40pm **NS+AS+SP-MoA5 Nano-photonic Phenomena in van der Waals Heterostructures**, *Dmitri Basov*, University of California San Diego
INVITED

Layered van der Waals (vdW) crystals consist of individual atomic planes weakly coupled by vdW interaction, similar to graphene monolayers in bulk graphite. These materials can harbor superconductivity and ferromagnetism with high transition temperatures, emit light and exhibit topologically protected surface states. An ambitious practical goal is to exploit atomic planes of vdW crystals as building blocks of more complex artificially stacked heterostructures where each such block will deliver layer-specific attributes for the purpose of their combined functionality. We investigated van der Waals heterostructures assembled from atomically thin layers of graphene and hexagonal boron nitride (Hbn). We observed a rich variety of optical effects due to surface plasmons in graphene and hyperbolic phonon polaritons in Hbn. We launched, detected and imaged plasmonic, phonon polaritonic and hybrid plasmon-phonon polariton waves in a setting of an antenna based nano-infrared apparatus. Peculiar properties of hyperbolic phonon polaritons in Hbn enabled sub-diffractive focusing in infrared frequencies. Because electronic, plasmonic and phonon polaritonic properties in van der Waals heterostructures are intertwined, gate voltage and/or details of layer assembly enable efficient control of nano-photonic effects. I will also discuss an ability to manipulate plasmonic response of in these structures at femto second time scales that we have demonstrated using a novel technique of pump-probe nano-infrared spectroscopy.

4:20pm **NS+AS+SP-MoA7 Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy and Fluorescence of a Self-Assembled Porphyrin Monolayer**, *Naihao Chiang**, *N. Jiang*, Northwestern University, *D. Chulhai*, Pennsylvania State University, *E. Pozzi*, *M.C. Hersam*, Northwestern University, *L. Jensen*, Pennsylvania State University, *T. Seideman*, *R.P. Van Duyne*, Northwestern University

The study of ultrahigh vacuum tip-enhanced Raman and fluorescence spectroscopy (UHV-TERS/TEF) has been raised to an unprecedented level. UHV-TER and TEF spectra for a self-assembled meso-tetrakis-(3,5-di-tertiarybutylphenyl)-porphyrin (H_2TBPP) on Ag(111) have been observed with five different laser excitations in the Q-band region. The observed TERS spectra are complemented by the time-dependent density functional theory (TDDFT) simulations. Chemical information of different vibronic excited states is revealed. The observed TEF spectra suggest a weak coupling of H_2TBPP to the surface due to the t-butyl groups. Therefore, the strong tip-enhancement is sufficient to overcome the quenching effect of the metal substrate. This study demonstrates the potential of combining TERS and TEF for studying surface-mounted porphyrins, thus setting the stage for future investigation into porphyrin-based photovoltaics and photocatalysis.

4:40pm **NS+AS+SP-MoA8 Nano-Optical Spectroscopic Imaging of Monolayer MoS_2** , *Wei Bao**, UC Berkeley, *N. Borys*, Lawrence Berkeley National Lab, *C. Ko*, *J. Suh*, *W. Fan*, UC Berkeley, *A. Thron*, Lawrence Berkeley National Lab, *Y. Zhang*, *A. Buyanin*, UC Berkeley, *J. Zhang*, *S. Cabrini*, *P. Ashby*, *A. Weber-Bargioni*, Lawrence Berkeley National Lab, *S. Tongay*, Arizona State University, *S. Aloni*, *D. Ogletree*, Lawrence Berkeley National Lab, *J. Wu*, UC Berkeley, *M.B. Salmeron*, Lawrence Berkeley Lab, UC Berkeley, *P. Schuck*, Lawrence Berkeley National Lab

With their remarkable electrical and optical properties, two dimensional (2D) monolayer transition metal dichalcogenide (ML-TMDC) semiconductors are ideal building blocks for atomically thin, flexible optoelectronic devices. Yet their performance falls far below theoretical expectations, particularly for critical factors such as carrier mobility and quantum yield. Overcoming these problems requires a fundamental understanding of the optoelectronic properties of these materials at the nanoscale, which is best obtained with optical microscopy and spectroscopy tools with spatial resolution below the diffraction limit. Here, we use the recently-developed "Campanile" nano-optical probe to spectroscopically image for the first time key optoelectronic properties in ML- MoS_2 with deeply sub-wavelength resolution – i.e., at a resolution commensurate with characteristic distances such as the exciton diffusion length. We find that synthetic ML- MoS_2 is composed of two distinct optoelectronic regions: a locally-ordered but mesoscopically heterogeneous interior, where photoluminescence (PL) intensity correlates with the local ratio of the exciton and trion populations, and an unexpected edge region $\sim 300\text{ nm}$ wide

* NSTD Student Award Finalist

of energetically disordered states. In addition, we directly visualize the spatially-varying optical properties of inter- and intra- flake grain boundaries and quantify the characteristic length over which they quench excitons. Complimentary Nano-Auger elemental analysis reveals that the optically “defective” grain boundary and edge regions are sulfur-deficient. The nanoscale structure-property relationships established here have broad implications for the development of atomically thin transistors, quantum optical components, photodetectors and light-emitting devices based on high-quality ML-TMDCs.

1 Bao, W. Mapping local charge recombination heterogeneity by multidimensional nanospectroscopic imaging., 1317-1321 (2012).

5:00pm **NS+AS+SP-MoA9 Hybrid Peak-force Tapping/near-field s-SNOM Microscope for Nano-chemical and Nano-mechanical Imaging of Proteins and Other Nanoscale Systems**, *Martin Wagner*, Bruker Nano Surfaces, *K. Carneiro*, *S. Habelitz*, University of California, *T. Mueller*, Bruker Nano Surfaces

Infrared spectroscopy can give valuable information on chemical composition, but far-field techniques such as FTIR spectroscopy are limited in spatial resolution. S-SNOM is a well-established near-field technique [1] that can overcome this diffraction limit, allowing an improvement in spatial resolution down to 10 nm.

Our s-SNOM instrument is based on an atomic force microscope whose tip is illuminated with a quantum cascade laser. Field-resolved detection of the scattered light measures absorption [2]. We have combined the instrument with peak-force tapping, a technique that allows Pn-level force control between tip and sample. Besides being able to image fragile material systems, one can extract valuable nano-mechanical information such as adhesion or modulus with molecular resolution [3].

Here, amongst other brief examples, we study an amelogenin sample. Amelogenin is a protein that is critical to dental enamel formation [4,5]. In the presence of calcium and phosphate ions it self-assembles into ordered, self-aligned nanoribbon bundles. Since the ordering is similar to the one observed in phosphate-based apatite crystals that comprise dental enamel, it is likely that the bundles form a template for these crystals. To help clarify that open question, we map the distributions of phosphate and hydroxyapatite nanocrystals within the bundles consisting of <30 nm narrow nanoribbons that have only a height of a few nm down to 1nm.

We present correlated topography, near-field and nano-mechanical data. While the presence of phosphate could be identified using s-SNOM absorption maps, no apatite nanocrystals with higher modulus than the ribbons were observed in peak-force tapping. This indicates that for these in vitro preparation conditions apatite crystals have not formed yet, but also highlights the high chemical sensitivity of the instrument.

In summary, using a novel combination of near-field imaging and peak-force tapping we study the phosphate distribution and crystallization in protein samples. Our findings help to understand the formation processes of dental enamel and the role of amelogenin protein.

[1] F. Keilmann, Hillenbrand R., Phil. Trans. R. Soc. Lond. A 362, 787 (2004)

[2] X. Xu, A. Tanur, G. Walker, J. Phys. Chem. A 117, 3348 (2013)

[3] F. Rico, C. Su, S. Scheuring, Nano Lett. 11, 3983 (2011)

[4] O. Martinez-Avila et al., Biomacromolecules 13, 3494 (2012)

[5] B. Sanii et al., J Dent Res 93 (9), 918 (2014)

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