



3rd Annual European Forum on Nanoscale IR Spectroscopy

National Physical Laboratory | London, UK
12 – 13 September 2018

<https://www.bruker.com/events/2018/efns.html>

This year Anasys is proud to be partnering with National Physical Laboratory to host the event, where attendees will be able to address the impacts of nanoIR spectroscopy in the fields of materials, life sciences, polymers and more.

Dean Dawson

Organization Committee



2018 EFNS Conference Attendee Information

Dear EFNS Attendee,

We are looking forward to seeing you at the 2018 EFNS conference at the National Physical Laboratory, Teddington, London UK on Wednesday/Thursday, September 12nd/13th.

To help with your travel planning and organization, please find information below regarding EFNS.

Please do not hesitate to contact us for further information or assistance.

We look forward to welcoming you in London and wish you excellent conference.

Best regards,

Yan Liu

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EFNS Program

Wednesday, 12 September

- 09:00** Registration: Coffee & pastries available
- 10:00** Welcome and Introduction
Dr. Alexander Tzalenchuk – NPL Fellow, National Physical Laboratory
- 10:10** Welcome, program review & logistics
Dean Dawson - Bruker/Anasys
- 10:30** Polymeric nanoparticle chemical analysis using Tapping AFM-IR
Prof. Alex Dazzi – Université Paris-Sud
- 11:15** Correlative Imaging of physical and chemical properties at the nanoscale with PeakForce Tapping
Dr. Chanmin Su – Bruker Nano Surfaces
- 12:00** Lunch
- 13:00** Chemical and structural characterisation of amyloidogenic inclusions in C. Elegance models of neurodegeneration | ***Dr. Francesco Simone Ruggeri – University of Cambridge***
- 13:35** AFM-IR Analysis of Solid Insulation Degradation
Dr. Suzanne Morsch – University of Manchester
- 14:10** Nano-scale hybrid structure molecular analysis
Prof. Dr. Ir. Tom Hauffman - Vrije Universiteit Brussel
- 14:45** Live demonstration/Tour/Coffee Break (rotating groups)
- 16:35** Leave for Evening Tour
- 17:00** Hampton Court Palace Visit (Transport will be arranged)
- 19:00** Conference Dinner (Transport will be arranged)
- 21:00** End Dinner (Transport arranged back to hotels)



EFNS Program

Thursday, 13 September

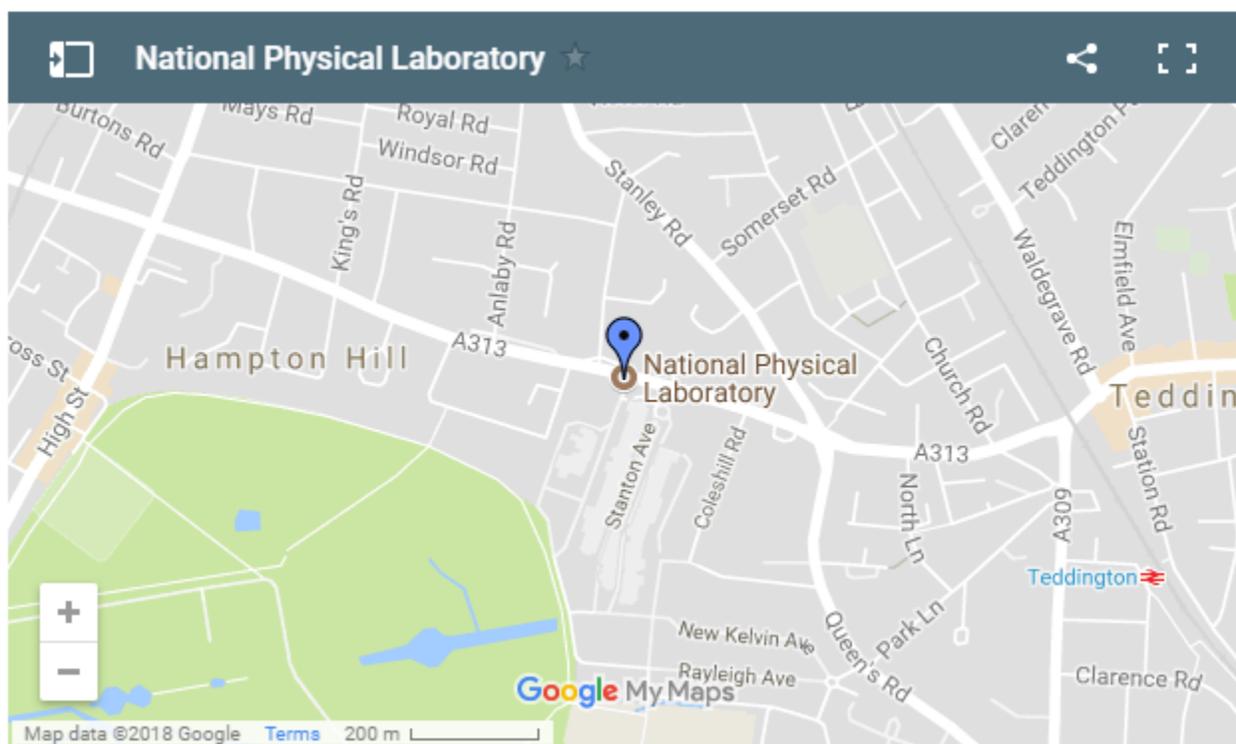
- 09:00** Registration: Coffee & pastries available
- 09:15** Advancements in nanoscale IR Spectroscopy
Dr. Curtis Marcott - Light Light Solutions
- 09:50** The Subcellular Structure of Eukaryotic Cells as Seen by AFM-IR Spectroscopy and Imaging
Dr. Luca Quaroni - Jagiellonian University
- 10:25** Coffee Break
- 11:00** Light-induced functional conformational changes of protein receptors probed by mid-IR nanospectroscopy | ***Dr. Valeria Giliberti – Italian Institute of Technology***
- 11:35** Beyond classical insight into nanoworld spectroscopy with nanoIR2
Prof. Dr. Hab. Wojciech Kwiatek - Institute of Nuclear Physics, Polish Academy of Sciences
- 12:10** Lunch
- 13:00** Poster session
- 13:45** When AFM-IR goes to interstellar space - a study of organic matter in an Antarctic micrometeorite
Jérémie Mathurin – Université Paris-Sud
- 14:20** Future developments in nanoscale IR spectroscopy
Dean Dawson – Bruker Nano/Anasys Instruments
- 15:00** Conference Close



EFNS Location & Access to the Venue

Address: National Physical Laboratory, Teddington, UK - TW11 0LW

NPL is in Teddington and a link to the map is located below.



Please note you will need some form of identification. Please enter the NPL site using the gate in Hampton road and follow instructions given by security. Directions can be found in the link below. Parking is not available unless booked in advance. It is recommended you catch a taxi or other forms of transport to get to NPL. Information and guidance for visitors is also available in this link.

<http://www.npl.co.uk/contact-us/location/>

Registration & Hotel Accommodation:

Please arrive at the reception on the morning of the conference. Registration commences at 9am, the conference starts at 10am. Coffee and pastries will be served during this time.



If you have not already booked hotel accommodation, please see the following accommodation suggestions:

- Alexander Pope <https://www.alexanderpope.co.uk/> (5 mins by car)
- Lensbury <http://www.lensbury.com/> (7mins by car)
- Doubletree3 Hilton <http://doubletree3.hilton.com/en/index.html> (10 mins by car)
- Bushy Park Lodge <http://www.bushyparklodge.co.uk/> (4 mins by car)

Group Activity and Dinner:

On Wednesday evening, there will be a tour at the Hampton Court Palace and then a group dinner directly after. Transportation is arranged from NPL and back to some local hotels. Some additional transportation may be required for people living further away.

Please note there is not really an option to go back to the hotel prior to departure, unless you decide to opt out of a tour of NPL labs.

Please let us know if you have any questions and we are looking forward to seeing you there.



Event Contacts

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Oral Presentations

Wednesday, 12 September 10:30

Polymeric nanoparticle chemical analysis using Tapping AFM-IR

Alex Dazzi

Université Paris-Sud

A.Dazzi¹, J.Mathurin¹, E. Pancani², A. Deniset-Besseau¹, R. Gref², K. Kjoller³, C.B. Prater³

1. Laboratoire de chimie Physique, Université Paris-Sud, 91405 Orsay - France
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3. Anasys Instruments, 325 Chapala Street, CA 93101 Santa Barbara -USA

The AFM-IR technique is a very powerful and efficient technique to chemically characterize materials at the nanometer scale [1]. Recent improvements in mid IR lasers and AFM techniques have further extended the capabilities of this technique. AFM-IR is based on coupling a tunable infrared laser and an AFM (Atomic Force Microscope). This coupling allows performing ultra-local infrared spectroscopy and chemical mapping at the nanometer scale. The principle is based on the detection of the sample thermal expansion, irradiated at the wavelength of its absorption bands. The applications of this infrared nanoscope are numerous from biology to polymer science [1]. In this talk, we will present a new mode of imaging and spectroscopy allowing analysis of soft and or adhesive samples: the tapping AFM-IR. This approach combines the resonance AFM-IR [2], with tapping mode imaging to provide a new system with high sensitivity and lateral resolution able to probe a broad range of samples, including nanoparticles or soft samples.

To exemplify the capabilities of this new technique, we will present results from the study of biodegradable polymeric nanoparticles. These nanoparticles are mainly used in nanomedicine as a drug delivery system. They appear to be a good alternative to overcome the problems encountered by antibiotics penetrating the cell membrane and increase the targeting of resistant bacteria. Unfortunately, there is a lack of knowledge about the chemical structure of these nanoparticles and the estimation of the amount of antibiotic inside the particles. The tapping AFM-IR technique is perfectly suited to answer these open questions and will help to fully characterize the polymeric nanoparticles.

[1] A.Dazzi, C.B. Prater, Chem. Rev. (2016).

[2] F. Lu, M. Jin, M.A. Belkin, Nat. Photon. 8, 307–312 (2014).



Oral Presentations

Wednesday, 12 September 11:15

Correlative Imaging of Physical and Chemical Properties at The Nanoscale with PeakForce Tapping

Chanmin Su

Bruker Nano

Xiaoji Xu¹, Martin Wagner¹ and Chanmin Su¹

1. Bruker Nano, 112 Robin Hill Road, Santa Barbara, CA 93003

PeakForce Tapping has been successfully applied in mapping nanoscale physical properties, primarily mechanical and electric properties, of broad range materials. This presentation focuses on extension of the technique, namely PeakForce IR, to chemical mapping based on photothermal effect. The key element in PeakForce IR is precise control of the spatial and temporal relationship of the tip-sample interactions, allowing opto-mechanical measurements synchronized to the proximate contact or transient contact zones. Mechanical or electric properties can also be derived at the same location in the synchronized measurements. We will provide use cases in oil rich shale and polymers with rough surfaces which are usually difficult for contact and tapping mode imaging, illustrate how the correlative data sets help to study complex materials at the nanoscale.



Oral Presentations

Wednesday, 12 September 13:00

Chemical and structural characterisation of amyloidogenic inclusions in *C. Elegans* models of neurodegeneration

Francesco Simone Ruggeri

University of Cambridge

Francesco Simone Ruggeri¹, Michele Perni¹, Chris M. Dobso¹, Michele Vendruscolo¹, Tuomas Knowles¹

1. Department of Chemistry, University of Cambridge, CB21EW United Kingdom

Misfolding and aggregation of mutated protein with polyglutamine (polyQ) expansions into fibrillar cross- β sheet amyloids is central in the pathogenesis of several inherited neurodegenerative disorders. This mutation triggers aggregation into nuclear inclusions bringing to the degeneration of striatal and cortical neurons. Despite the worldwide scientific effort, the increased toxicity of polyQ-expanded aggregates and the aetiology of disease remains incompletely understood, besides there is contrasting evidence in favor of a protective or a toxic role of the inclusions in pathogenesis. This uncertainty exists mainly because the characteristic heterogeneity and nanoscale dimensions of amyloid pathological aggregates preclude to current biophysical and immunochemistry assays a profound investigation of the correlation between the amyloidogenic nature of inclusions in human tissue and molecular mechanism of toxicity.

Here, in order to overcome this scientific gap, we use the Infrared Nanospectroscopy (AFM-IR) technique to study at the nanoscale the chemical and conformational state of single inclusions in intact *C. Elegans* worms, which are a widely exploited animal model to study degeneration. First, we compare the chemical and structural properties of inclusions in healthy and pathogenic aging worm, showing that a clear amyloidogenic signature can be identified. Then, we study the state of inclusions upon treatments of the worms with pharmacological treatments that can restore their state of health. This information would be key to evaluate the efficacy of pharmacological approaches in modifying the amyloid structure of the inclusions in the brain.



Oral Presentations

Wednesday, 12 September 13:35

AFM-IR Analysis of Solid Insulation Degradation

Suzanne Morsch

University of Manchester

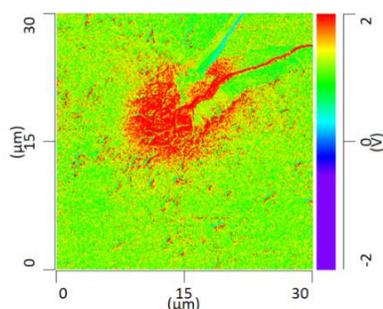
Suzanne Morsch^{1*}

Harry McDonald², Pablo Bastidas², Simon Rowland²

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2. School of Electrical and Electronic Engineering, The University of Manchester, Manchester, UK

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AFM-IR is used to provide new insights into the degradation mechanism of polymeric insulation under electrical stress. Highly cross-linked network polymers (XLPE, epoxies and composites) are increasingly used in high voltage cabling owing to their excellent breakdown strengths and dielectric properties. To enable the continued development of power transmission cabling, an understanding of the chemical processes resulting in failure, most notably electrical treeing and electrical tracking, is essential. Unfortunately, during these processes, highly localized reactions produce degradation products which lie beyond the detection limits of analytical techniques commonly used to investigate such phenomena (e.g., optical and fluorescence microscopy, XPS, ESR, and conventional vibrational spectroscopy/microscopy). Here, AFM-IR is used to provide chemical analysis beyond visible damage ordinarily used to characterize failure. Two cases are considered; that of interfacial tracking between epoxy and silicone rubber, and the characterization of a degraded region formed around the needle tip during electrical tree initiation. Local infrared analysis revealed oxidation of the epoxy resin, which has previously been associated with the formation of interfacial tracks or tree channels (detected by ATR-FTIR), in fact occurs far beyond the visibly damaged regions ordinarily used to characterize reaction progression.



30 μm x 30 μm AFM-IR image showing carbonyl groups produced around a needle tip embedded in epoxy resin immediately after initiation of electrical treeing.

[1] S. Morsch, P. D. Bastidas, and S. M. Rowland, "AFM-IR Insights into the Chemistry of Interfacial Tracking," *Journal of Materials Chemistry A*, vol 5, pp. 24508-24517, 2017.

[2] H. McDonald, P.D. Bastidas, S.M Rowland, and S. Morsch "Chemical Analysis of Solid Insulation Degradation using the AFM-IR Technique", in preparation.



Oral Presentations

Wednesday, 12 September 14:10

Nano-scale hybrid structure molecular analysis

Tom Hauffman

Vrije Universiteit Brussel

T. Hauffman, F.

Cavezza, S. Pletincx, A. Cruz, R. Ameloot, H. Terry

Hybrid structures, where an organic component is combined with an inorganic one, are omnipresent in today's society. The applications range from coatings on metal structures to high-end metal-organic frameworks for semi-conductor appliances.

The nanoscale boundary between the organic and inorganic phase is crucial as this has a major impact on the durability and efficiency of the system. Nano-IR enables us to characterize with a high lateral resolution the bonding variety of organic molecules on various alloys. Furthermore, using FIB cross-sections, we are able to visualize buried interfaces and look at inter-phase molecular changes due to various metal pretreatments and atmospheric conditions.

On the other hand, nano-IR is used for the characterization of the molecular and phase structure of metal-organic frameworks. A novel set-up, using an all vapour synthesis method, leads to the creation of porous hybrid crystalline materials. The synthesis temperature, precursors used and reaction time lead to various chemistries and phase structures. Nano-IR enables us to unravel these reaction specific morphologies and chemistries, leading to process optimization.



Oral Presentations

Thursday, 13 September 09:15

Advancements in nanoscale IR Spectroscopy

Curtis Marcott

Light Light Solutions

Anirban Roy¹,

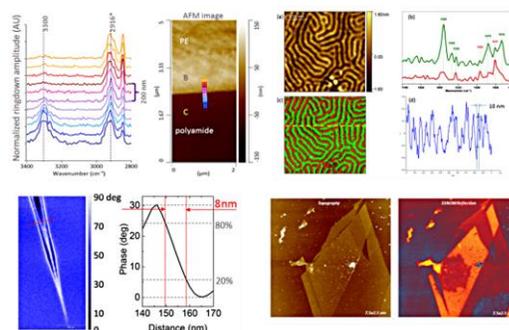
Qichi Hu¹, Honghua Yang¹, Miriam Unger¹ and Curtis Marcott²

1. Bruker Nano Surfaces, Santa Barbara, CA 93117, USA

2. Light Light Solutions, LLC, Seabrook Island, SC 29455, USA

For the last few decades the rapid growth in the field of nanoscience and technology has led to the development of new characterization tools for nanoscale materials. Traditional IR and Raman spectroscopy and imaging offers excellent chemical insights, however, the spatial resolution is limited by the optical diffraction limit ($\sim\lambda/2$). Although, recent Super-resolution microscopy techniques [1, 2] offer superior spatial resolution, they are primarily implemented in fluorescence imaging, hence needs external fluorophore tag for detection. Alternatively, nanoscale IR spectroscopy/imaging offers a “tag free” spectral detection with high spatial resolution beyond optical diffraction limit (2-5 μm) by exploiting an AFM probe [3] to detect either photothermal expansion force (PTIR) or near field scattered IR light (sSNOM).

Recent developments in PTIR and sSNOM technology have significantly augmented the speed and spatial resolution for chemical analysis. One of the new developments (Tapping AFM-IR) allows acquisition of IR images at a specific absorption band simultaneously with sample topography and nano-mechanical properties, providing a complete set of topographical, chemical and mechanical insights with <10 nm spatial resolution. These high resolution measurements are currently accompanied by high speed tunable laser enabling fast point spectral acquisition (1-2 ms/spectrum) leading to hyperspectral data cube for rigorous statistical analysis similar to Chemometrics applications.



In this presentation, we will highlight the technical background and applications of these emerging technologies in different fields, e.g., nanomaterials, life sciences, polymers, microelectronics etc.

[1] B. Huang, M. Bates, X. Zhuang, *Annu. Rev. Biochem.*, 78, 993-1016 (2009).

[2] T. D. Harris, R. D. Grober, J. K. Trautman, and E. Betzig, *Appl. Spectro.*, 48, 14A-21A (1994).

[3] A. Dazzi and C.B. Prater, *Chem. Rev.*, 117, 5146-5173 (2016)



Oral Presentations

Thursday, 13 September 09:50

The Subcellular Structure of Eukaryotic Cells as Seen by AFM-IR Spectroscopy and Imaging

Luca Quaroni

Jagiellonian University

Luca Quaroni^{1,2} * Katarzyna Pogoda², Joanna Wiltowska-Zuber², Wojciech Maria Kwiatek².

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Atomic Force Microscopy – Infrared (AFM-IR) spectroscopy allows spectroscopic studies in the mid-infrared spectral region with spatial resolution better than allowed by diffraction. [1] The high spatial resolution allows studies of eukaryotic cells with subcellular spatial resolution. We use fixed fibroblast cells to demonstrate the use of the technique in spectromicroscopy and imaging of vesicles, micelles, organelles and the cytoskeleton. We show that the technique allows imaging with intrinsic contrast and chemical characterization of specific subcellular structures. By using 1650 cm⁻¹ excitation, corresponding to the Amide I absorption peak of proteins, we observe fibrillar structures that we assign to the polymerized actin filaments of the cytoskeleton. This is the first observation of such structures by AFM-IR inside a cell. By using 2920 cm⁻¹ excitation, at the absorption peak of long acyl chains, we observe a range of micelles and lipid droplets distributed throughout the cytoplasm and ranging in size from about 100 nm to more than 1000 nm. Excitation at 1740 cm⁻¹, corresponding to the peak absorption of phospholipid ester carbonyls, provides additional images of vesicles, micelles and other micrometric structures that may be organelles or fragments of stacked membranes. We also record IR absorption spectra of individual particles and vesicles. The spectrum displays contributions from both phospholipid and protein components, as expected for proteoliposome-type particles. We discuss these observations in terms of the properties of individual organelles, cellular biochemistry and the chemistry of the fixation process.

[1.] A. Dazzi and C.B. Prater. Chem. Rev (2016). 10.1021/acs.chemrev.6b00448



Oral Presentations

Thursday, 13 September 11:00

Light-induced functional conformational changes of protein receptors probes by mid-IR nanospectroscopy

Valeria Giliberti

Italian Institute of Technology

Valeria Giliberti¹

1. Istituto Italiano di Tecnologia, Center for Life Nanoscience (CLNS-IIT), Rome (Italy)

The permeability of lipid bilayer of biological membranes to a variety of ions and molecules is conferred by protein receptors that act as pumps and channels in response to specific stimuli. The transport of ions and molecules through the membrane is made possible by a sequence of protein conformational changes, and mid-IR spectroscopy is commonly regarded as one of the basic tools to investigate such functional conformational changes [1]. In this work, we apply the photo-thermal induced mechanical resonance platform (AFM-IR) to the investigation of the light-induced conformational changes of bacteriorhodopsin (BR), i.e. a paradigm for those transmembrane proteins acting as pumps of molecules under absorption of visible photons. We perform differential IR nanospectroscopy (visible light ON-visible light OFF) of BR embedded in its native purple membrane, probing a relative variation of the absorption spectrum A of the order of $(A_{ON}-A_{OFF})/A_{OFF} \approx 0.01$. The use of an AFM-IR setup [2] enables us to observe the subtle conformational changes of BR embedded in two overlapping purple membranes whose area is less than $1 \mu\text{m}^2$, with a dramatic increase of sensitivity compared with standard mid-IR spectroscopy [3]. Our results open the way to novel experimental schemes addressing the IR vibrational spectroscopy of light-sensitive protein receptors embedded in their native intrinsically heterogeneous cell membranes, rather than purified and embedded in reconstructed lipid bilayers as typically done for standard IR spectroscopy.

[1] E. Ritter et al., *Front Mol Biosci.* 2, 38, 2015

[2] V. Giliberti et al., *Small*, 13, 1701181, 2017

[3] K. Atake et al., *Biochim. Biophys. Acta (BBA)-Biomembranes*, 1828, 2283-2293, 2013



Oral Presentations

Thursday, 13 September 11:35

Beyond classical insight into nanoworld spectroscopy with nanoIR2

Wojciech Kwiatek

Institute of Nuclear Physics, Polish Academy of Sciences

W. M. Kwiatek

E. Lipiec, C. Paluszkiwicz, N. Piergies, E. Pięta, K. Pogoda

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Infrared nanospectroscopy combines nanoscale resolution of AFM and chemical selectivity of molecular spectroscopy; therefore it is very efficient tool in studies of plethora biochemical problems. The use of nanoIR2 system allows us to cover broad range of applications from nanomaterials to biological samples. We have successfully implemented such methodology to study (i) a correlation between heterogeneous chemical composition and 3D structure of nanotubes [1], (ii) the behaviour of a drug adsorbed on a metal substrate at the nanoscale level [2], (iii) structural differentiation of normal and cancer cells [3], and (iv) the chemical composition of lipid droplets synthesised in glioblastoma cells upon ionizing radiation exposure [4]. Each of these applications will be discussed in detail based on the studies performed at the Laboratory of Spectroscopic Imaging for Radiobiology, Therapy, and of complex systems research at the Institute of Nuclear Physics Polish Academy of Sciences.

[1] A. Mikhalchan, A. M. Banas, K. Banas, A. M. Borkowska, M. Nowakowski, M. B. H. Breese, W. M. Kwiatek, C. Paluszkiwicz, T. E. Tay, *Chem. Mater.* 2018, 30, 6, 1856-1864.

[2] N. Piergies, E. Pięta, C. Paluszkiwicz, H. Domin, W. M. Kwiatek, *Nano Research* 2018, DOI: doi.org/10.1007/s12274-018-2030-z.

[3] E. Pięta, K. Pogoda, M. Woźniak, J. Zuber-Wiltowska, C. Paluszkiwicz, W. M. Kwiatek, in preparation.

[4] E. Lipiec, B. R. Wood, A. Kulik, W. M. Kwiatek, G. Dietler, *Anal. Chem.* 2018, under review.



Oral Presentations

Thursday, 13 September 13:45

When AFM-IR goes to interstellar space - a study of organic matter in an Antarctic micrometeorite

Jérémie Mathurin

Université Paris-Sud

Jérémie Mathurin¹, Emmanuel Dartois², Cécile Engrand³, Ariane Deniset¹, Christophe Sandt⁴, Ferenc Borondics⁴,
Thomas Pino², Jean Duprat³, Alexandre Dazzi¹

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2. Institut des sciences moléculaires d'Orsay, CNRS, Univ. Paris Sud, Université Paris-Saclay, F-91405 Orsay, France

3. Centre de Sciences Nucléaires et de Sciences de la Matière (CSNSM), CNRS/IN2P3, Univ. Paris Sud, Université Paris-Saclay, F-91405 Orsay, France

4. Synchrotron Soleil, L'Orme des Merisiers, BP48 Saint Aubin, 91192 Gif-sur-Yvette Cedex, France

Primitive extra-terrestrial objects are the witnesses of the nascent protoplanetary disk around the young sun, billions years ago. Coming from different regions of our Solar system, micrometeorites are the record of past nebular processes and give access to the origins of the solar system and the disk evolution. Before planets formation, dust grains size distribution lies in the few ten to hundreds nanometre range. Micrometeorites contain aggregates of such particles.

A small fraction of the Antarctic micrometeorites from the Concordia-CSNSM collection are rich in organic matter (OM): the UltraCarbonaceous Antarctic MicroMeteorites (UCAMMS), also found in other collections. These OMs dominated micrometeorites most likely come from the surface of small icy bodies in the outer regions of the solar system. This considerably higher organic fraction enables direct analyses without the pre-treatment generally applied to extract the organic phase in other meteoritic samples and give access to unaltered chemical information.

Variations of the organic composition of the UCAMMs are best studied by looking at the distribution of the different chemical bonds using infrared vibrational spectroscopy. However, classical infrared technique is limited by the diffraction, with typical spot sizes sampling a few micrometres range in the mid-infrared. Even if it provides an unrivalled global view of the dust grain chemical structure content, the resolution remains limited and doesn't give access to the intimate structure of the sample compared to other techniques such as isotopic imaging with NanoSIMS or elemental electron imaging techniques whereas these techniques don't give directly access to the distribution of the different chemical bonds. This problem was solve using AFM-IR microscopy to go beyond this diffraction limit [1].

By mapping organic matter without pre-treatments, and tracing quantitatively the different forms of organic matter constituting the dust grains, we demonstrate in this study it is mandatory to go under the diffraction limits using AFM-IR microscopy to understand the chemical functional group diversity of such objects. In this presentation we will also talk about what kind of issues can appears when studying new kind of objects such Antarctic micrometeorite with the AFM-IR technique.

[1] Mathurin J. et al, Astronomy and Astrophysics, under review



Posters

Spectroscopic nano-imaging of plasmons for nanoscale, calibration-free measurement of graphene Fermi energy

W.S. Hart

Imperial College London, UK

Mapping drugs inside single cells without labelling using mid-infrared nano-imaging

W.S. Hart

Imperial College London, UK

Nanoscale Chemical Imaging in Service of CNT Fiber Nanocomposites Analysis

Agnieszka Banas

Singapore Synchrotron Light Source NUS

Processing of AFM-IR chemical mapping results of carbon nanotube composite materials in R Environment

Krzysztof Banas

Singapore Synchrotron Light Source NUS

Characterisation of self-assembled protein capsules by correlative nano-IR microscopy and spectroscopy

Ibolya Kepiro

Bruker Nano Surfaces

Unravelling Protein Aggregate Structure at the Nanoscale by AFM-IR

Francesco Simone Ruggeri

University of Cambridge



Spectroscopic nano-imaging of plasmons for nanoscale, calibration-free measurement of graphene Fermi energy

W. S. Hart[†], V. Panchal^{||}, Włodek Strupiński[‡], C. Melios^{||}, O. Kazakova^{||} and C. C. Phillips[†]

[†]Department of Physics, Imperial College London, UK [‡]Faculty of Physics, Warsaw University of Technology, Warsaw, Poland ^{||}National Physical Laboratory, Teddington, UK

The Fermi energy of graphene plays a central role in many of its applications, particularly in plasmonics. Common methods for measuring the Fermi energy, such as the Hall effect, are limited to spatially averaging over the entire graphene device. In 2012, it was first shown that graphene plasmon nano-imaging could be used to map the dispersion of plasmons. This utilises a scattering-type scanning near-field optical microscope (s-SNOM) to actively launch plasmons in graphene and detect their self-interference. Here, we present wide-band plasmon nano-imaging using tuneable quantum cascade lasers as a means to measure the local Fermi energy of hydrogen-intercalated graphene, 298 ± 4 meV. In doing so, we map the dispersion curve of graphene plasmons over more than an order of magnitude of plasmon wavelength, from $\lambda_{sp} \sim 140$ to ~ 1700 nm. This technique works in atmospheric conditions and requires no calibration. Furthermore, we demonstrate the appearance of wavelength tuneable plasmon reflection “hotspots” at single-layer/bi-layer graphene interfaces. Such hotspots could be designed via manipulation of bi-layer graphene geometry, for use in enhanced chemical analysis, environmental monitoring, and as plasmonic nano-antennas for boosting the sensitivity of fluorescence microscopy and vibrational spectroscopy



Mapping drugs inside single cells without labelling using mid-infrared nano-imaging

W. Hart^{1,*}, H. Amrania¹, A. Beckley², J. Brandt³, S. Sundriyal³, A. Zubiaurre³, A. Porter⁴, M. Fuchter³, E. Aboagye², C. Phillips¹

¹Experimental Solid State Group, Department of Physics, Imperial College London, London, SW7 2AZ, UK

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³Department of Chemistry, Imperial College London, London, SW7 2AZ, UK

⁴Department of Bioengineering, Royal School of Mines, Imperial College London, London, SW7 2AZ, UK

Mid-IR spectroscopy ($\lambda \sim 5\mu\text{m}$ to $12\mu\text{m}$) is widely used to identify chemicals. It exploits the fact that molecules absorb light at certain frequencies that are particular to their structure. Traditional methods have high spectral resolution, but are diffraction limited to large spatial resolutions of $\sim 10\mu\text{m}$, and so can only allow for the study of groups of cells, for example. IR nano-imaging offers a way of beating the diffraction limit. S-SNOM uses an extremely sharp ($\sim 10\text{nm}$ radius) probe, close to a sample. The probe scatters light in such a way that the optical information is collected in a region only $\sim 10\text{nm}$ in diameter. The tip is raster scanned across the specimen to produce an optical image with resolution of $< \lambda/1000$ in the mid-IR. Until now this has only been used for controlled solid state systems. Using a new range of widely-tuneable mid-IR lasers (QCLs), it is now possible to map chemical composition of unaltered samples at unprecedented (nanometric) spatial resolution. This poster will include examples of nanoscale mapping of the anti-cancer drug bortezomib within a single human myeloma cell, as well as infrared nano-imaging of sub-cellular organelles.



Nanoscale Chemical Imaging in service of CNT Fiber Nanocomposites analysis

Anastasiia Mikhalchan^{1*}, Agnieszka M. Banas², Krzysztof Banas², Anna M. Borkowska³, Michal Nowakowski³, Mark B. H. Breese², Wojciech M. Kwiatek³, Czeslawa Paluszkiwicz³, Tong Earn Tay¹

¹ Department of Mechanical Engineering, National University of Singapore, 117576 Singapore

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³ Institute of Nuclear Physics, Polish Academy of Sciences, PL-31342 Krakow, Poland

The unique fibrous assemblies made of carbon nanotubes (CNT) have been developed in early 2000's. CNT fibers consist of hundreds thousands carbon nanotube bundles entangled together and aligned along the fiber's axial direction. Through their distinguished hierarchical structure, it is possible to utilize all unique properties of individual carbon nanotubes (extremely high strength, stiffness, electrical and thermal conductivity etc.) in a broad range of novel materials with advanced functionality. An interesting and promising feature of the CNT fibers is their yarn-like and highly porous structure, formed from its composition of 104 to 105 CNT bundles per cross section. However, in terms of practical applications involving the intrinsic porous structure of CNT fibers, there are not much scientific understanding of their infiltration processes by other molecules, either polymeric or not. It seems that CNT fibers should be infiltrated with a monomer that could be subsequently cross-linked or polymerized within the sub-micron voids. All the processes that happen during the infiltration of the CNT fiber and curing of a polymer in the nano-structural porous CNT 'scaffold' are of great interest and practical importance.

In our work, the advanced imaging capabilities of the AFM-combined infrared spectroscopy (AFM-IR) has been implemented, for the first time, to analyse the CNT fibre-reinforced thermoset nanocomposite.

Intricate chemical structure and thin polymer interphase forming within the CNT assembly during the composite processing have been detected with the high resolution of sub-30 nm. As an example, we unravel the chemical information exclusively from the CNT bundles and visualize it in conjunction with morphology in a two- and three-dimensional format. We furthermore introduce a contact frequency map co-localized with CNTs and surrounding polymer, which might correlate the local mechanical properties with polymer chemistry and the high anisotropy of CNTs. With this research, we envision the AFM-IR spectroscopy as an exceptional characterization tool for the next-generation materials and devices based on CNT assemblies.



Processing of AFM-IR chemical mapping results of carbon nanotube composite materials in R Environment

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Nanostructural composites reinforced with carbon nanotube assemblies, such as CNT fibres and mats are interesting materials for the multiple potential applications: from avionics to high-tech industry. Possibility to gain insight into the chemical composition of such materials may provide a way for their further development and improvement of manufacturing process.

By combining infra-red spectroscopy (IR) and atomic force microscopy (AFM) it is possible to perform the chemical mapping with the spatial resolution down to 30 nm. The CNT nanocomposites were analysed by means of nanoIR2 system (Anasys Instruments, USA). Due to technique specific method of the detection of the infrared signal special attention must be paid during data-processing stage. Obtained results were evaluated with the help of R - open source environment for statistical analysis in order to ensure interpretability and reproducibility of the collected data. Various modes of measurements were processed, visualised and correlated to gain a better understanding of the system under investigation. Particularly the problem of obtaining topography-free infrared absorbance signal is discussed and some possible solutions are suggested in this contribution.

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Characterisation of self-assembled protein capsules by correlative nano-IR microscopy and spectroscopy

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Protein self-assembly provides an effective strategy for the construction of high-performance materials, components and devices for a variety of biomedical applications ranging from capsular materials for drug delivery to scaffolds for regenerative medicine. Despite a significant progress made in recent years in the area, an unambiguous physio-chemical characterisation of self-assembled materials remains both challenging and critical for the development of functionally more complex designs. High-resolution imaging methods such as atomic force microscopy (AFM) and transmission electron microscopy (TEM) can provide important insights into the micro- and ultra-structure of self-assembled architectures at the nanoscale. However, these measurements lack information related to the chemical composition of the materials. Providing and correlating chemical information with that of physical properties of self-assembled materials holds promise for more advanced technologies with higher performance values. Here, we present our recent results in characterising bespoke protein capsules by correlated nano-IR microscopy and spectroscopy. The protein capsules presented here are polydisperse, hollow nanoscale shells specifically designed for drug and gene delivery. Their morphologies and topographic architectures were characterised by TEM and AFM and were correlated with their chemical compositions investigated by nanoscale IR absorption spectroscopy (AFM-IR) and scanning near-field optical microscopy (SNOM), which provided complementary images used to map the distribution of specific chemical signatures over the surface of capsule samples. The results show the importance of correlative analysis in drug development to measure and monitor secondary and higher-order structures as changes in the structure can impact the safety, stability and quality of protein therapeutics losing their biological function.



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