

EFNS 2022

5th European Forum on Nanoscale IR Spectroscopy

September 6th -8th, 2022 | TU Wien | Vienna, Austria



Preface

Bruker and TU Wien are pleased to announce that EFNS 2022 will be held September 6-8 in the beautiful city of Vienna. EFNS connects leading scientists in the field of nanoscale infrared spectroscopy and imaging.

This interactive forum benefits everyone interested in the IR nanoscale chemical and physical characterization of polymers, life sciences, 2D materials, and micro-electronics. The program is designed to facilitate information sharing so that it is valuable for experts and novices alike. It includes oral presentations, poster competitions, system demonstrations at a workshop on September 8th and the possibility to talk to Bruker experts in person.

Attendees can expect to discover new technology developments and exciting application discoveries made using photothermal-based nanoIR and scattering SNOM spectroscopy and imaging.

Conference Host

Prof. Dr. Bernhard Lendl and Dr. Georg Ramer
Institute of Chemical Technologies and Analytics, TU Wien, Vienna, Austria

Conference Venue

TU Wien, Campus Getreidemarkt
Getreidemarkt 9, 1060 Vienna, Austria

Conference Organizational Contacts

Miriam Unger, Bruker, Germany
Annette Niedballa, Bruker, Germany

Practical Information

EFNS 2022

EFNS 2022 is held at the TU Wien, located in the beautiful city of Vienna. EFNS, Bruker's European Forum on Nanoscale IR Spectroscopy, includes oral presentations from leading research groups, as well as live demonstrations and discussions with Bruker experts. For additional information, please visit the conference website at <https://www.bruker.com/efns-conference>.

Oral Presentation Guidelines

Please prepare your presentation in 16:9 format and provide your slides as PPTX file to our technical support staff in the morning of your presentation.

Contributed talks are 12 minutes in length, with an additional 3 minutes for discussion.

Invited talks are 25 minutes, with an additional 5 minutes for discussion.

Poster Presentation Guidelines

Posters should be prepared in A0 portrait format; stands and pins will be provided.

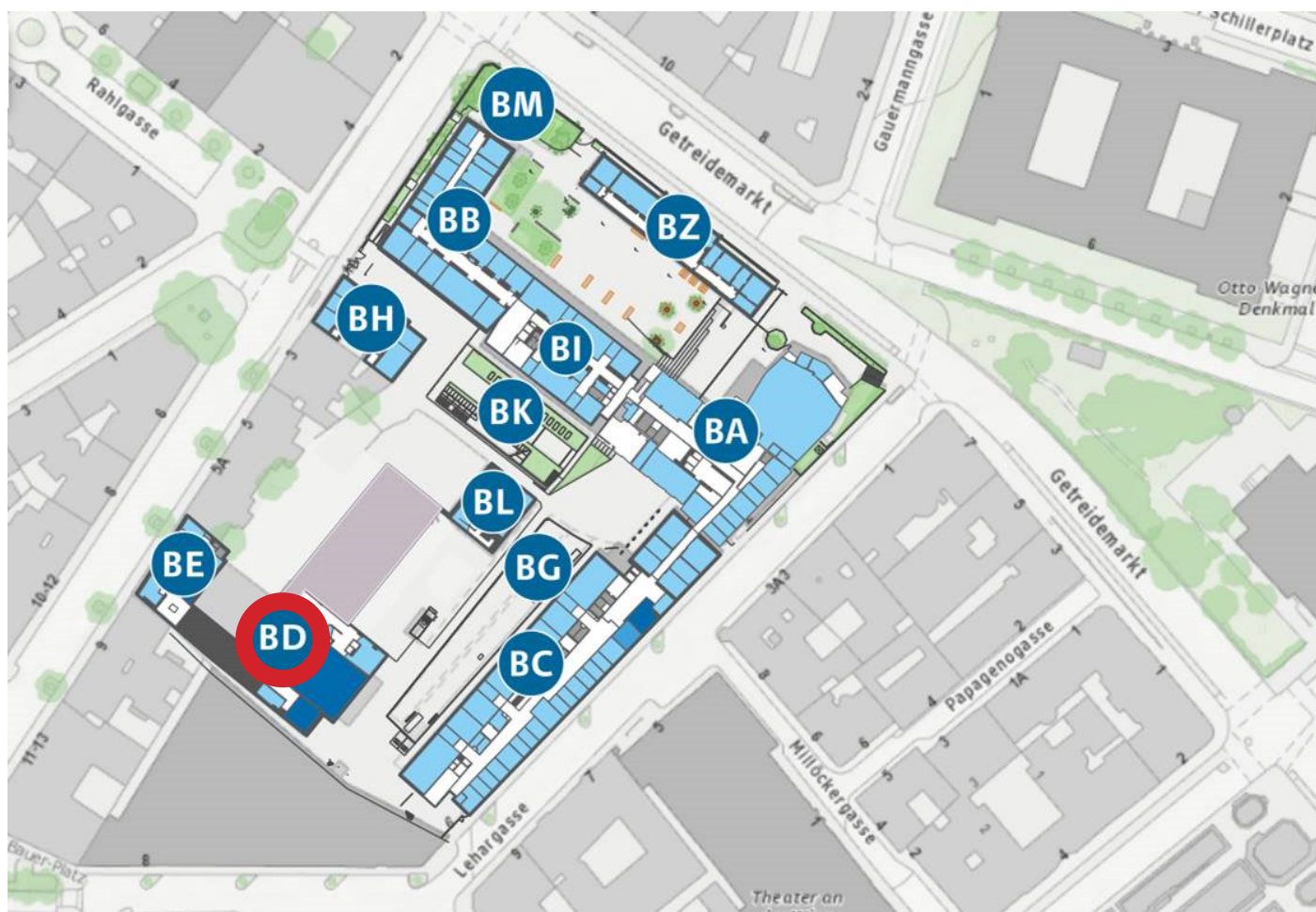
Conference Venue

TU Wien, Campus Getreidemarkt
Getreidemarkt 9, 1060 Wien, Austria

EFNS Conference Room: GM2, "Radinger", located in "BD" Building

Entrance via: Lehartgasse 6, 1060 Wien

Poster Session & Catering: GM 8/9, located in "BD" Building



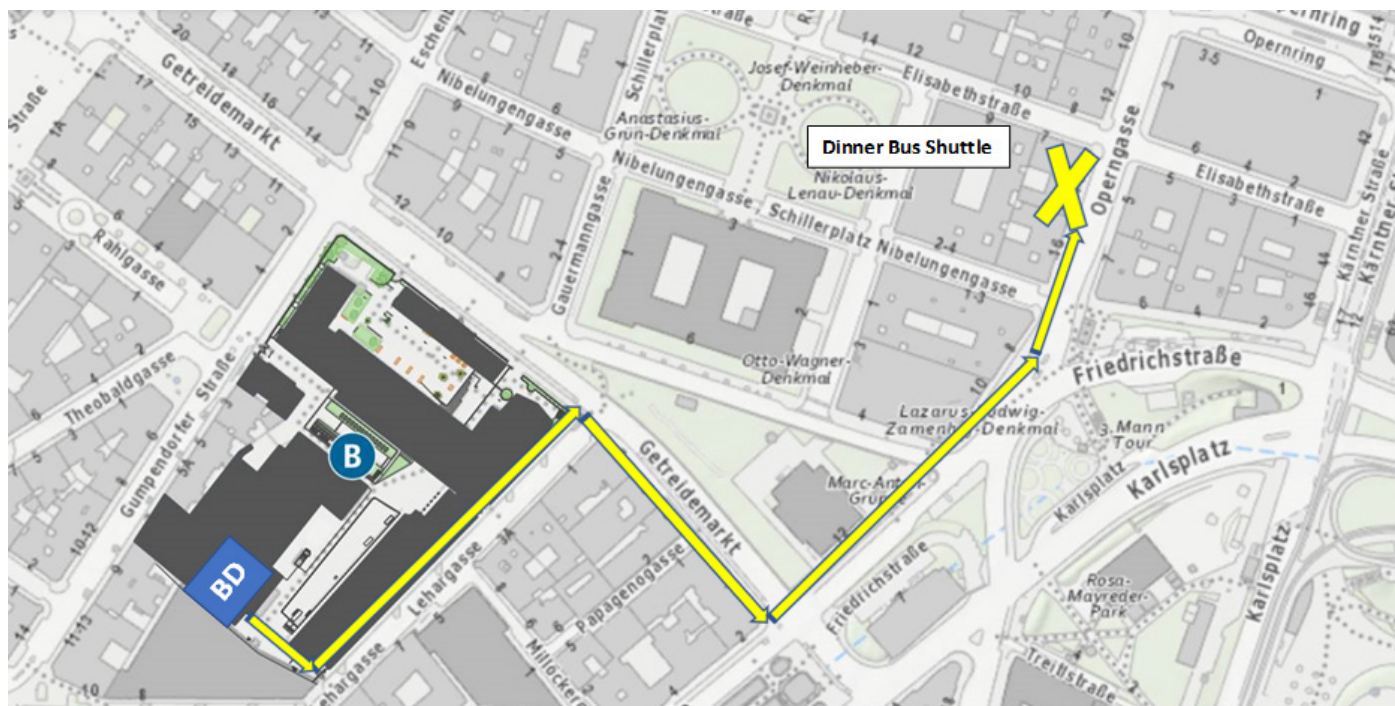
EFNS Conference Dinner – 6 September, 19:30

Mayer am Pfarrplatz
Pfarrplatz 2
1190 Wien

The EFNS Conference Dinner will be held in the “Mayer am Pfarrplatz” winery, the epitome of Viennese Heuriger culture.

Bus shuttle to Conference Dinner

The shuttle to the "Mayer am Pfarrplatz" winery leaves at 19:00, please make sure to arrive early! The bus shuttle will start from Operngasse 14 (approx. 5 min walk from EFNS conference, 1 min walk from Motel One Vienna Staatsoper).



Social Event - City Rally – 7 September, 18:00-20:00

Join in on our evening excursion. We will explore the historic city center in this quiz rally. The rally will start 18:00 at Stephansplatz (next to the entrance of the St. Stephen's cathedral).

Day 1: Tuesday, September 6th

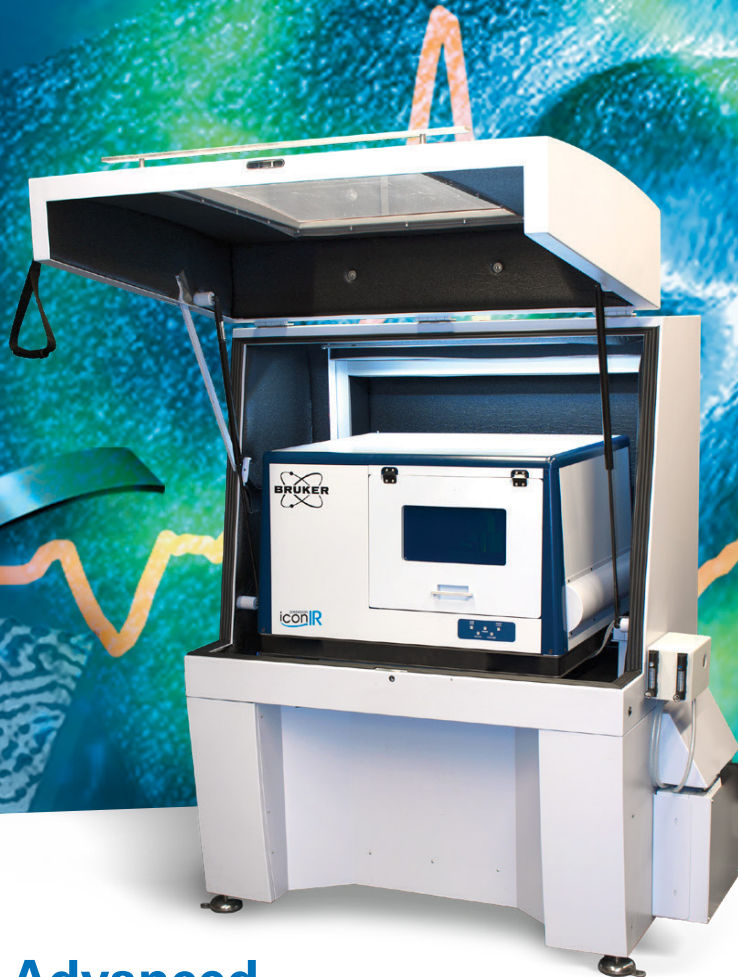
- 08:00 Registration
- 09:15 Welcome & Introduction
- 09:30 What's new in photothermal AFM-IR at BRUKER?
- 10:00 Photothermal AFM-IR surface sensitive mode
Prof. Dr. Alexandre Dazzi, Université Paris-Saclay, France
- 10:30 **BREAK**
- 11:00 AFM-IR analysis of extraterrestrial materials: from micrometeorites to Ryugu samples
Dr. Jérémie Mathurin, Université Paris-Saclay/CNRS, France
- 11:30 AFM-IR spectroscopy of natural samples: from coals to the asteroid belt
Prof. Dr. Pierre Beck, Université Grenoble Alpes, France
- 12:00 **LUNCH**
- 13:00 Coexistence of multiple prion conformers: IR nanospectroscopy to investigate the degree of secondary structure polydispersity
Prof. Dr. Ariane Deniset-Besseau, Université Paris-Saclay, France
- 13:30 More than 10 years of nano-chemical analysis: where now, where next?
Road to single-molecule and in-situ characterization by AFM-IR
Dr. Francesco Simone Ruggeri, Wageningen University, Netherlands
- 14:00 Mid-infrared nanospectroscopy of individual DNA-binding protein oligomers
Valeria Giliberti, Istituto Italiano di Tecnologia (IIT), Rome, Italy
- 14:15 AFM-nanoIR spectroscopy and imaging of DNA molecules on mica surface
Eric Lesniewska, University of Bourgogne Franche-Comté, Dijon, France
- 14:30 Characterization of secondary structure of protein by infrared nanospectroscopy
Jehan Waeytens, Université libre de Bruxelles, Belgium & Université Paris-Saclay, France
- 14:45 **POSTER SESSION**
- 16:15 Structure characterization in plastics technology using photothermal excited Atomic Force Microscopy
Prof. Dr. Marc Kreutzbruck, University of Stuttgart, Germany
- 16:45 Investigation of polymer surface and interface by nanoTA and nanoIR
Prof. Dr. Tung Pham, University of Innsbruck, Austria
- 17:15 Characterization of welding seams from amorphous thermoplastics using nanoscale IR-Spectroscopy
Julia Dreier, University of Stuttgart, Germany
- 17:30 AFM-IR application in chemical industry: case of polymer blends
Ouissam Abbas, ExxonMobil, Machelen, Belgium
- 17:45 Correlating molecular segregation to epoxy interphase formation with AFM-IR
Dr. Suzanne Morsch, University of Manchester, United Kingdom
- 18:15 End of day 1
- 19:30 **CONFERENCE DINNER**

Day 2: Wednesday, September 7th

- 09:15 **Micro to Nano: a multi-scale IR spectroscopy studies of metal soaps in oil paints**
Prof. Dr. Xiao Ma, Shanghai University, China
- 09:45 **Vibrational spectroscopy at the nanoscale: from art history to high performance polymer blends**
Dr. Mike Casford, University of Cambridge, United Kingdom
- 10:15 **Application of tapping-mode AFM-IR to a post-consumer waste Polyolefin recyclate**
A. Catarina V. D. dos Santos, TU Wien, Vienna, Austria
- 10:30 **BREAK**
- 11:00 **Detecting evolution and properties of bitumen surface microstructures at different environmental conditions: AFM-IR and NanoTA**
Dr. Farrok Tarpoudi Baheri, EMPA, Switzerland
- 11:30 **AFM-IR for nanoscale degradation assessment in industrial coil coatings**
Alexander Wärnheim, RISE & KTH Royal Institute of Technology, Sweden
- 12:00 **LUNCH**
- 13:00 **Surface enhancement in AFM IR technique and its application in drug/metal nanocarrier characterization**
Dr. Natalia Piergies, Polish Academy of Sciences, Poland
- 13:30 **From prism to flat silicon: Novel approach for AFM-IR measurements in liquids**
Ufuk Yilmaz, TU Wien, Vienna, Austria
- 13:45 **Infrared polarimetry to study the anisotropy of polymer nanofiber**
PD Dr. Karsten Hinrichs, ISAS – e.V., Germany
- 14:15 **Towards a point spread function for nanoscale chemical imaging**
Yide Zhang, TU Wien, Vienna, Austria
- 14:30 **Advanced probing of light-matter interaction at nanoscale for quantum optoelectronics**
Dr. Nathaniel J. Huang, National Physical Laboratory, United Kingdom
- 15:00 **BREAK**
- 15:30 **Exploiting infrared light-matter interaction for deterministic and tunable nanomachining of 2D materials**
Prof. Dr. Laurene Tetard, University of Central Florida, USA
- 16:00 **s-SNOM as an interrogation technique of optical modes of plasmonic metamaterials for novel applications in SPDC in the mid-IR**
Mayela Romero-Gómez, National Physical Laboratory, United Kingdom
- 16:15 **Study of steaming effects of ZSM-5 zeolite using AFM-IR technique**
Denys V. Benedis, Université Paris-Saclay & IFP Energies nouvelles, Solaize, France
- 16:30 **Tiny Data: Nanoscale hyperspectral imaging**
Dr. Georg Ramer, TU Wien, Vienna, Austria
- 17:00 **Closing**
- 18:00 **SOCIAL EVENT**

Day 3 - nanoIR Workshop: Thursday, September 8th

| | |
|-------|---|
| 09:30 | Crash course nanoIR: Theory, Instrumentation and Applications |
| 10:45 | BREAK |
| 11:00 | Photothermal AFM-IR (live demo and Q&A) |
| 12:00 | LUNCH BREAK |
| 13:00 | Photothermal AFM-IR in liquid (live demo and Q&A) |
| 14:30 | End of Workshop |



World's Most Advanced Photothermal IR Spectroscopy Solutions

Bruker's nanoscale infrared (nanoIR) spectrometers measure spatially varying physical and chemical properties in a diverse range of fields, from polymers and 2D materials to life science and micro-electronics. Fueling an impressive and growing publication record, these systems are advancing academic discovery and helping industrial companies solve critical process problems.

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Poster List — Ordered by last name of presenting author

- 1. Electrical transport dynamics of conducting polymers under nanoconfinement**
Sukanya Das, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India
- 2. Towards in situ and in vitro AFM-IR studies of neurodegenerative disease**
Wouter Duverger, KU Leuven, Belgium
- 3. Applications of AFM-IR in polymer industry**
Cecilia Fabris, ExxonMobil, Machelen, Belgium
- 4. Direct visualization of the drug loading of single DNA Origami nanostructures by AFM-IR nano-spectroscopy**
Marcel Hanke, Paderborn University, Germany
- 5. Chemical spectroscopy of individual human milk extracellular vesicles**
Nikolaus Hondl, TU Wien, Vienna, Austria
- 6. Photothermal AFM-IR unveils nanoscale features and chemical information of wood cell walls**
Kavindra Kumar Kesari, Aalto University, Espoo, Finland
- 7. Detecting the influence of inter-particle proximity on the catalytic properties of NPs**
Mazal Kostan, The Hebrew University of Jerusalem, Israel
- 8. Nanoscale characterization of single chiral polymer chains**
Xuecong Li, Wageningen University & Research, Wageningen, Netherlands
- 9. Nanochemical microscopy of polymer systems: limitations and peculiarities**
Mikhail Malanin, IPF Dresden, Germany
- 10. Multicomponent covalent chemical patterning of Graphene: AFM-IR for chemical characterization of nanometer-thick layers of functional groups**
Kunal S. Mali, KU Leuven, Belgium
- 11. Too small to succeed: Why enhanced resonance AFM-IR cannot easily detect nano-objects**
J. Mathurin, Univ. Paris-Saclay/CNRS, Orsay, France
- 12. AFM-IR analysis in human breast tissue to decipher breast microcalcifications genesis and potential link with cancer**
Margaux Petay, Université Paris-Saclay, Orsay, France
- 13. New insight of Orgueil C11 chondrites using nano-IR spectroscopy**
Van T. H. Phan, Université Grenoble Alpes/CNRS-INSU, UMR 5274, Grenoble, France
- 14. AFM-IR studies of cysteine adsorption behavior on the Au nanoparticles-titanium surfaces**
Natalia Piergies, Institute of Nuclear Physics Polish Academy of Sciences, Krakow, Poland
- 15. Novel AFM-IR analysis applied to cultural heritage samples**
Ellen Purdy, University of Cambridge, UK
- 16. Miscibility and phase separation in PMMA/SAN blends investigated by nanoscale AFM-IR**
Julia Resch, University of Stuttgart, Germany
- 17. Identifying reactivity variations on different facets in single Au nanocrystals**
Lihl Rikanati, The Hebrew University of Jerusalem, Israel
- 18. Nanophotonic transducer for AFM-IR**
Savda Sam, Munster Technological University, Bishopstown, Cork, Ireland
- 19. Surface modification of titanium by Cu nanoparticles in the presence of amino acid**
Dominika Świąch, AGH University of Science and Technology, Krakow, Poland

Talk Abstracts

Day 1, Tuesday, September 6th

10:00 | Photothermal AFM-IR surface sensitive mode

Alexandre Dazzi¹, Jérémie Mathurin¹, Ariane Deniset-Besseau¹.

¹Institut de Chimie Physique – Université Paris-Saclay – 91400-ORSAY – France

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The photothermal AFM-IR technique is becoming in less than ten years a reference technique for infrared nanoscale analysis. AFM-IR is an atomic force microscopy (AFM) based technique that combines the high spatial resolution of AFM with the chemical identification capability of infrared (IR) spectroscopy. The field of applications is really wide and cover scientific domains like molecular biology, polymer science, microbiology, medicine, geology, culture heritage, astrochemistry [1].

Up to now the operating modes of photothermal AFM-IR are the same than classical AFM (contact, tapping and peakforce) allowing to study a large range of different sample.

Recently, we have developed and patented a new operating mode intrinsic to the photothermal AFM-IR technique to only probe the first nanometers below the surface in opposite to the hundreds of nanometers detected by the contact mode. This new mode is called 'surface sensitive' [2] and allow to open new perspective of infrared nanoscale analysis like identification of surface contamination even if the bulk materials is absorbing in the same infrared range or the possibility to switch from resonance enhanced to the surface sensitive AFM-IR mode to probe different depth on the sample area. For example the figure below shows how the surface sensitive mode is clearly more accurate to perfectly localize the droplets of PS (polystyrene) inside a PMMA (poly methyl methacrylate) matrix compared to the resonance enhanced (contact) mode.

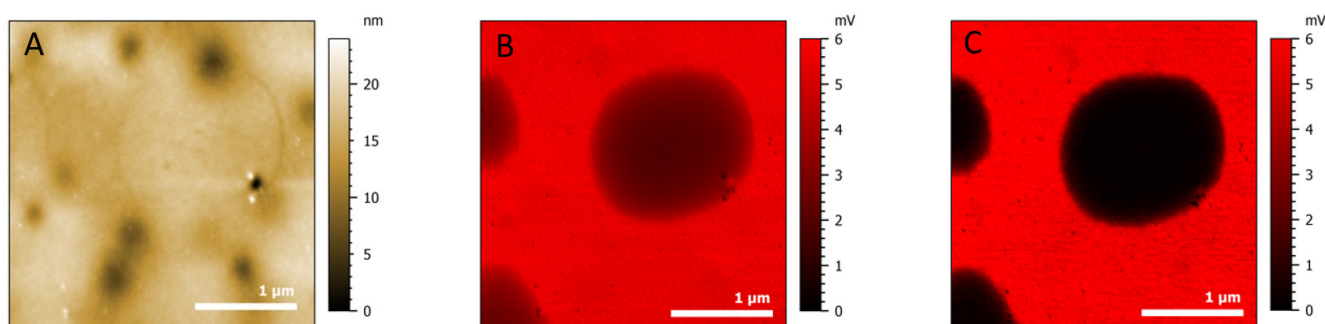


Figure: A) PMMA-PS blend topography. B) Chemical mapping at 1730 cm^{-1} corresponding to the ester carbonyl band of PMMA in resonance enhanced AFM-IR (contact) mode where PMMA is still detected under the PS bead. C) Chemical mapping at 1730 cm^{-1} corresponding to the ester carbonyl band of PMMA in surface sensitive AFM-IR mode where the PS area shows no absorption.

[1] A. Dazzi, C.B. Prater, Chem. Rev., 117, 7, 5146–5173, (2017).

[2] J. Mathurin et al. J. Appl. Phys, 131, 010901 (2022).

11:00 | AFM-IR analysis of extraterrestrial materials: from micrometeorites to Ryugu samples

Mathurin J.¹, Dartois E.², Dazzi A.¹, Deniset-Besseau A.¹, Bejach L.³, Engrand C.³, Duprat J.⁴, Kebukawa Y.⁵, Yabuta H.⁶, Yurimoto H.⁷, Nakamura T.⁸, Noguchi T.⁹, Okazaki R.¹⁰, Naraoka H.¹⁰, Sakamoto K.¹¹, Tachibana S.^{11,12}, Watanabe S.¹³, Tsuda Y.¹¹ and the Hayabusa2-initial-analysis IOM and STONE teams

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The distribution of chemical bonds in organic matter (OM) of interplanetary samples (meteorites and micro-meteorites) can be efficiently and non-destructively characterized at the scale of a few μm using infrared (IR) vibrational spectroscopy [1]. Since a few years, AFM-IR is used to circumvent the spatial resolution diffraction limit of conventional IR spectroscopy allowing to access the distribution of chemical bonds at the sub-micron scale. In 2019, we first study UltraCarbonaceous Antarctic MicroMeteorites (UCAMMs) that are dominated by OM and thus do not need chemical (acid) treatment prior to the analyses. In this study, we demonstrated the possibility to unravel chemical heterogeneity of these particles OM [2]. From this pioneering work, we improved sample preparation and analytical method opening the possibility the direct study OM in extraterrestrial samples containing only few percents of carbon. We applied these methods to various samples including chondritic meteorites [3] and the precious samples from asteroid Ryugu returned by the Hayabusa2 JAXA mission, that we received from the "IOM" and "Stone" initial analysis teams led by Dr. H. Yabuta and Dr. T. Nakamura, respectively [4], [5]. Both on chondritic meteorites and Ryugu samples, AFM-IR measurements demonstrate the presence of organic inclusions intimately mixed with minerals at the sub-micron scale [4]. Focusing on the OM-rich zones of Ryugu samples, it is possible to unveil in situ heterogeneities in the IR signature of the chemical bondings in the OM, such as local C=O enrichment within spots sizes of a few tens of nm.

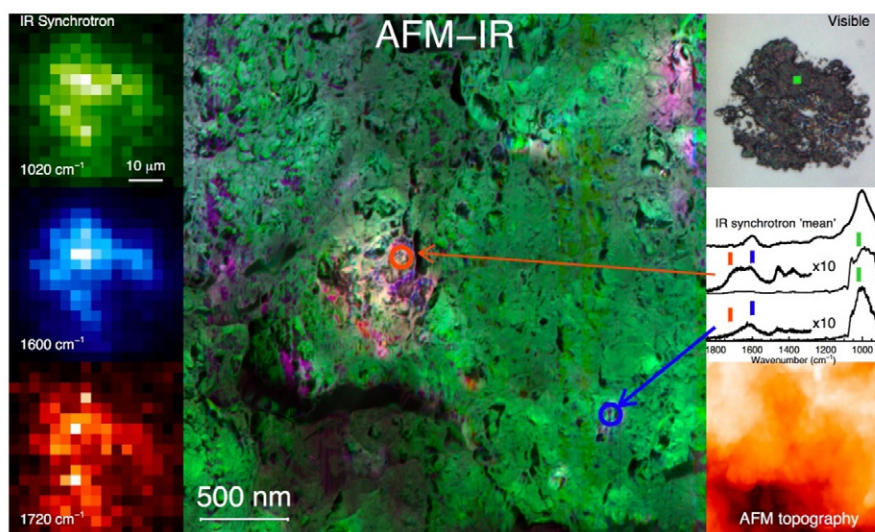


Figure 1. AFM-IR study of chamber C sample C109-04, in the context of μFTIR maps. Left panels: maps obtained by transmission synchrotron μFTIR and corresponding to the absorption of Si-O (silicates at 1020 cm^{-1} , green), C=C (1600 cm^{-1} , blue) and C=O (1720 cm^{-1} , red) – Middle panel: $3 \times 3\ \mu\text{m}$ RGB composite image combining the AFM-IR absorption mapping obtained at same wavenumber (and corresponding colors) as the μFTIR synchrotron maps – Right panels: Top: optical image of the crushed sample; Middle (from top to bottom spectra): average μFTIR synchrotron spectra obtained on the whole sample, local spectra obtained by AFM-IR highlighting the presence of OM with and without a C=O signature at 1720 cm^{-1} . The red, blue and green dashes indicate the wavenumber positions of the IR mapping with the same color; Bottom: AFM topography of the $3 \times 3\ \mu\text{m}$ area studied in AFM-IR. (Mathurin et al. 2022 LPSC).

- [1] E. Dartois et al., "Dome C ultracarbonaceous Antarctic micrometeorites," *Astron. Astrophys.*, vol. 609, p. A65, Jan. 2018.
- [2] J. Mathurin et al., "Nanometre-scale infrared chemical imaging of organic matter in ultra-carbonaceous Antarctic micrometeorites (UCAMMs)," *Astron. Astrophys.*, vol. 622, 2019.

- [3] I. Kerraouch et al., "Heterogeneous nature of the carbonaceous chondrite breccia Aguas Zarcas - cosmochemical characterization and origin of new carbonaceous chondrite lithologies"; GCA, accepted
- [4] H. Yabuta et al., "Macromolecular organic matter recording aqueous activity on the parent body of the asteroid Ryugu"; Science, under review
- [5] T. Nakamura et al., "Formation and evolution of Cb-type asteroid Ryugu: Direct evidence from returned samples"; Science, under review

11:30 | AFM-IR spectroscopy of natural samples: from coals to the asteroid belt

Pierre Beck^{1}, Van T.H. Phan², Rolando Rebois and Eric Quirico¹*

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By being able to break the diffraction limit, AFM-IR spectroscopy offers a great potential in material science. Natural samples that are often finely grained, are also a major field of applications, and the application of nano-optical-spectroscopy techniques to such natural and often complex material is expanding. In the IPAG group, under funding by the European Research Council, we are developing the application of AFM-IR to extra-terrestrial materials, in particular to the study of primitive meteorites and asteroid particles. We will present the development we made on sample preparation and analytical protocol on reference minerals and natural macromolecular organics (coals). We will also present our latest results obtained on the mineralogy, the structure of organics and their distribution at the sub- μm scale on a suite of primitive extra-terrestrial samples.

13:00 | Coexistence of multiple prion conformers: IR nanospectroscopy to investigate the degree of secondary structure polydispersity

J. Mathurin,¹ A. Dazzi,² D. Martin,² A. Igel,² J. Torent i Mas,² V. Beringue,² H. Rezaei², A. Deniset-Besseau,¹

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Prion diseases are transmissible, fatal and untreatable neurodegenerative diseases which are still a major health concern and threat. Actually, studies are limited by fundamental questions around the prion paradigm and more precisely by its molecular composition and replication process. During the pathology evolution, the host encoded monomeric protein called PrP_c is converted into misfolded aggregating conformers called PrP that self-replicate and self-organize in the brain through a molecular mechanism called templating. Thus, the prion pathology is based on autonomous structural information propagation towards single or multiple protein conformational changes.

The objective of our project is to decipher the process of prion replication at the molecular level, which would also be a breakthrough for prion-like diseases. Recently, we reported that prion replication is intrinsically source of structural diversification [1], [2]. The coexistence of multiple prion assemblies with different structural and replication propensity raise questions on prion assemblies self-organization and the conservation of its intrinsic variabilities. We propose here to study these questions using AFM-based techniques. AFM measurements show that assemblies have an overall fibrillar shape. However, numerous spherical protrusions are observed, either staked on the fibrils or in the vicinity of the fibres or as isolated objects. The secondary structures of these assemblies are then studied using AFM-IR [3], [4] and revealed at the single assembly's scale an intra-assembly's heterogeneity. As a consequence, rather than a canonical amyloid assembly, prion assemblies constitute a complex dynamic system far from the equilibrium where at least two different sub-populations coexist through catalytical material exchange.

References

- [1] A. Igel-Egalon et al., "Heterogeneity and architecture of pathological prion protein assemblies: Time to revisit the molecular basis of the prion replication process?," *Viruses*, vol. 11, no. 5, 2019.
- [2] A. Igel-egalon et al., "Crossing Species Barriers Relies on Structurally Distinct Prion Assemblies and their Complementation To cite this version : HAL Id : hal-03401965 Crossing Species Barriers Relies on Structurally Distinct Prion Assemblies and Their Complementation," 2021

- [3] A. Dazzi, R. Prazeres, F. Glotin, and J. M. Ortega, "Local infrared microspectroscopy with subwave length spatial resolution with an atomic force microscope tip used as a photothermal sensor," *Opt. Lett.*, vol. 30, no. 18, pp. 2388–2390, 2005.
- [4] D. Partouche et al., "Correlative infrared nanospectroscopy and transmission electron microscopy to investigate nanometric amyloid fibrils: prospects and challenges," *J. Microsc.*, vol. 274, no. 1, pp. 23–31, Apr. 2019.

13:30 | More than 10 years of nano-chemical analysis: where now, where next? Road to single-molecule and in-situ characterization by AFM-IR

Francesco Simone Ruggeri^{1,2}

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The introduction of photothermal infrared nanospectroscopy (AFM-IR) has revolutionized the field of nano-chemical analysis in a wide-open range of fields, including biological, material and polymer sciences. Here, we review discuss our latest technological developments of AFM-IR [1-4] and their successful advanced application to unravel puzzling questions at the nanoscale [5-10].

Where now?

In the last 10 years, we have pioneered AFM-IR to successfully unravel and correlate the morphological, mechanical, and chemical properties of materials and biomolecular systems, starting from large microfluidic prepared droplets [8] and living organisms [9] to down to the single monolayer [5] and remarkably thanks to the development of ORS-nanoIR down to the single molecule level [1].

Where next?

The sensitivity of AFM-IR has yet not reached the true ability to measure single molecule properties [1], and still mostly require operation in air. While we and other laboratories have demonstrated AFM-IR operation in liquid [10], in these conditions the method had even further limited sensitivity to samples of ~100 nm thickness. The development of these features will be crucial in the next years to transform and widen the application of AFM-IR as key analytical methods in Science.

[1] Ruggeri, *Nature Comm.*, 2020.

[2] Ruggeri, *Nature Comm.*, 2018.

[3] Ruggeri, *Nature Comm.*, 2021.

[4] Otzen, ..., Ruggeri, *Small Methods*, 2021.

[5] Marchesi, *Advanced Functional Materials*, 2020.

[6] Doherty, *Science*, 2021.

[7] Shen, Ruggeri, *Nature Nanotechnology*, 2020.

[8] Muller, *Lab on a Chip*, 2014.

[9] Ruggeri, *IJMS*, 2018.

[10] Ramer, Ruggeri, *ACS Nano*, 2018.

14:00 | Mid-infrared nanospectroscopy of individual DNA-binding protein oligomers

*A. Intze*¹, *M. E. Temperini*¹, *R. Polito*², *E. Zacco*³, *J. Rupert*³, *G. G. Tartaglia*³, *A. Pastore*⁴, *M. Ortolani*^{1,2} and *V. Giliberti*¹

¹ *Center for Life Nano- & Neuro-science, Istituto Italiano di Tecnologia (IIT), Rome, Italy*

² *Department of Physics, Sapienza University of Rome, Italy*

³ *Central RNA Laboratory, Istituto Italiano di Tecnologia (IIT), Genova, Italy*

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In the last decade, a breakthrough in the analysis of protein conformation well beyond the diffraction limit has been achieved with the introduction of IR nanospectroscopy methods based on the use of high resolution atomic force microscopy (AFM) [1-3]. Here we apply the photothermal expansion IR nanospectroscopy

(AFM-IR) to the study of the TAR DNA-binding protein 43 (TDP-43), the main pathological protein associated to Amyotrophic Lateral Sclerosis and Fronto Temporal Dementia. Fourier transform IR spectroscopy (FTIR) and FTIR-microspectroscopy are used to validate the general spectroscopic results as a function of time. In Fig. 1 we report preliminary AFM-IR results. The AFM-IR spectra acquired on individual oligomers (see Fig. 1a) were fitted over the entire 1450-1800 cm^{-1} range and, in the case of the amide I, we used five Lorentzian components centered at 1634, 1644, 1664, 1680, 1690 cm^{-1} . In Fig. 1b we plot the trend over time of the IR spectral weight (SW) of the amide I band components. An increase of the mean value of the SW attributed to β -sheet secondary structure element of the protein (see inset in Fig. 1b) is clearly observed, in agreement with what expected during the formation of protein aggregates. This general behavior is accompanied by structural heterogeneities probed at each sampling time, that can be probed only leveraging on the high-resolution of an AFM-based IR method. Further measurements and analysis are ongoing.

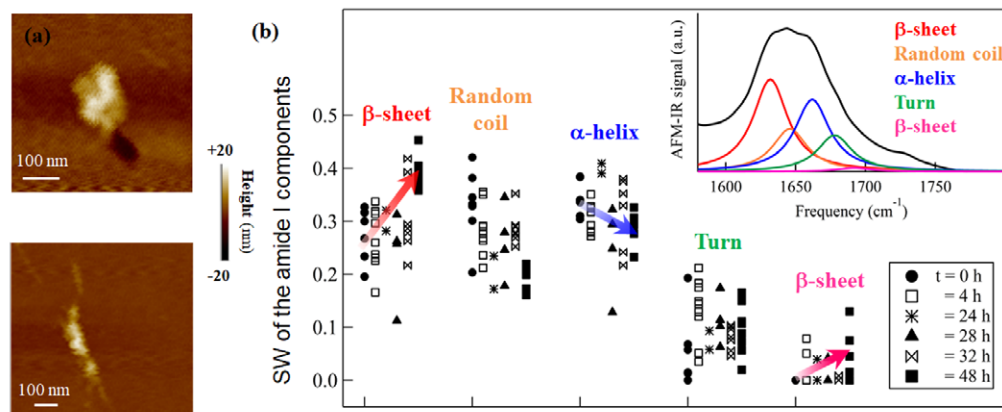


Fig. 1. (a) AFM topography maps of representative TDP-43 oligomers. (b) Trend over time (0 to 48 hours) of the relative infrared spectral weight (SW) of the amide I band components (inset). SW is calculated by dividing the spectral weight of each component by the sum of the spectral weight of the five components used to fit the amide I.

References

- [1] F. S. Ruggeri et al., Nat communications, vol. 6, no. 1, pp. 1-9, 2015.
- [2] V. Giliberti et al, Nano Letters, vol. 19, no. 5, pp. 3104-3114, 2019.
- [3] T. Dou et al., J. Phys. Chem. Lett. vol. 12, pp. 4407–4414, 2021.

14:15 | AFM-nanoIR spectroscopy and imaging of DNA molecules on mica surface

E. Lesniewska^{1*}, *I. Custovic*¹, *N. Pocholle*¹, *E. Bourillot*¹, and *O. Piétremont*¹

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Over the past decade AFM-IR technique has become a powerful approach for nanospectroscopic investigation of many biological systems and recently demonstrated its leverage through nanoscale chemical mapping at a single molecule level of studied protein^{1,2}. Here, we demonstrate first methodological approach for acquisition of AFM-IR chemical mapping modalities with corresponding absorption spectra based on two distinctly formed DNA morphologies on mica surface: condensed DNA network by spermidine and single DNA molecule formed upon Ni^{2+} pretreated mica surface. The nanoscale IR absorbance monitored through the series of AFM-IR absorption maps and acquired spectra show the characteristic absorbance band assigned to DNA-spermidine interaction for DNA network and absorption band assigned to vibrations of nucleobases for single DNA molecule. Our results³ thus demonstrate high sensitivity of AFM-IR nanospectroscopy for a nucleic acid research with an open potential to be employed in further investigation of multi-component DNA-protein assembly.

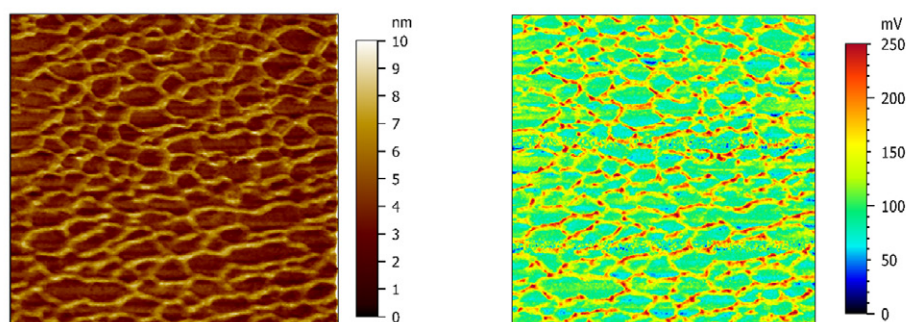


Figure 1 AFM-IR imaging of DNA network formed upon spermidine pretreated mica surface. Size of imaged area: 4 x 4 μm^2 . a) AFM topography image of DNA and corresponding b) AFM-IR absorption map of DNA network recorded at optimized wavenumber 1728 cm^{-1} showing DNA of higher absorbance (bright red porous contour) regarding to underlying mica surface.

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<https://doi.org/10.48550/arXiv.2201.12092>

14:30 | Characterization of secondary structure of protein by infrared nanospectroscopy

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During biological processes, protein conformation can change. A better understanding of those biological processes required a description of these conformational changes. Protein secondary structure is commonly studied by circular dichroism and Fourier transform infrared spectroscopy (FTIR). These spectroscopic techniques are versatile and can monitor those changes; they can be adapted to wide experimental conditions and are non-destructive.

FTIR is very useful for homogeneous sample as it can only provide an average spectrum even if different species are present. To overcome this limit, optical microscopy can be coupled with FTIR and spectra with a resolution of only a few micrometers can be obtained. More recently a technique coupling atomic force microscopy and infrared spectroscopy was developed (AFM-IR). It has a resolution of few nanometers and is therefore able to record spectra of single biomolecule.

So far, very little is known on the ability of AFM-IR to predict secondary structure of protein. Comparison between FTIR and AFM-IR were reported with good consistency between the two methods, but it was done for a limited number of proteins and using only curve fitting analysis method. We study a protein library of 38-well characterized proteins and developed a model of prediction for the secondary structure. This was done by comparing ascending stepwise linear regression and partial least square. Even if small differences are observed between FTIR and AFM-IR spectrum, our models of prediction have similar errors for AFM-IR and FTIR around 6 % for α -helix and β -sheet.

16:15 | Structure characterization in plastics technology using photothermal excited Atomic Force Microscopy

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Structural analysis techniques are widely used in plastics analysis for both in the context of research and development activities and also in areas of damage analysis or quality assurance. Atomic force microscopy based infrared spectroscopy (AFM-IR) is a novel technique that allows the combination of chemical analysis and compositional imaging with a spatial resolution far below the conventional optical diffraction limits. At the Institut für Kunststofftechnik, this technique is used for a wide variety of applications. The high spatial resolution of a few nm allows for the analysis of nanoplastics in environmental samples. Currently, the detection of small plastics particles using established methods such as IR-microscopy and Raman-analysis are limited to resolutions of 10 μm and 1 μm respectively. Nano-AFM-IR is now paving the way to shift this

limit down to a few nm. We also used the AFM to precisely analyze the morphology of various plastic blends. For example, the composition of miscible amorphous blends is studied where the chemical imaging allows to clearly differentiate the two blend partners from each other down to the nanometer range. We also report on welded joints and weld lines and their mechanisms of action as well as matrix adhesion and dispersion of fillers and additives, also with regard to new recycling materials.

16:45 | Investigation of polymer surface and interface by nanoTA and nanoIR

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Two examples are given in the talk. The first is the study of topochemical enzyme-catalyzed hydrolysis reaction on PLA fibers using nano-TA. Enzymatic hydrolysis preferentially occurs in the amorphous regions of the fiber outer layer, resulting in random hydrolysis, monomer release, and ablation of the fiber surface during the initial phase of hydrolysis. Since the accessibility of the enzyme to the fiber core is limited, the change in crystallinity occurs predominantly in the outer region of the fiber. The observed increase in surface softening temperature from the glass transition temperature to near the melting point of crystalline PLA detected with nano-TA supports the hypothesis of selective hydrolysis of the amorphous region at the fiber outer layer, resulting in modified PLA fibers with an unmodified fiber core and a very thin and highly crystalline surface layer.

The second study focuses on polymer diffusion at the interface between polyamide and polypropylene. By using the nano-IR technique, very detailed information about the formation of the interfacial layer is obtained. This allows the determination of the interfacial layer thickness as well as the observation and visualization of the diffusion gradient through the PA/PP interface. In combination with classical investigation methods such as interfacial energy and rheology, nano-IR spectroscopy represents a very powerful tool to gain more insight and a deeper understanding of interfacial phenomena in multiphase polymer systems.

17:15 | Characterization of welding seams from amorphous thermoplastics using nanoscale IR-Spectroscopy

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Welding is one of the most common joining methods in the production of plastic components. During welding, the macromolecules of the two joining partners form a joint across the interface. At the current state of the art, some criteria and models try to explain the mechanisms of action in a weld seam. Diffusion processes of individual molecular chains across the interface are assumed. However, the theories based on it could not yet be proven. Especially for amorphous thermoplastics, the analysis possibilities are very limited, since they do not have a long-range order. Welded joints of different amorphous thermoplastics were produced by hot plate welding and analyzed using nanoscale infrared spectroscopy. PMMA and SAN were selected as materials and successfully welded together. The AFM-IR was used to examine the welded joint and identify the weld seam and the two polymers.

17:30 | AFM-IR application in chemical industry: case of polymer blends

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Atomic force microscopy (AFM) coupled with (IR) spectroscopy has been increasingly used for the nanoscale chemical characterization of polymeric materials hence its use in the chemical industry as a reliable tool to characterize new developed materials and predict their final properties. The case of polymer blends is

challenging considering criteria such as miscibility, polymeric separation or chemical interactions between the blend constituents. This presentation will allow sharing our efforts to develop and optimize AFM-IR methods to characterize various blend polymers starting with probe selection, spectral quality optimization and data acquisition then treatment by correlating AFM images with chemical maps or via the application of chemometric tools to extract the significant information from the data set.

17:45 | Correlating molecular segregation to epoxy interphase formation with AFM-IR

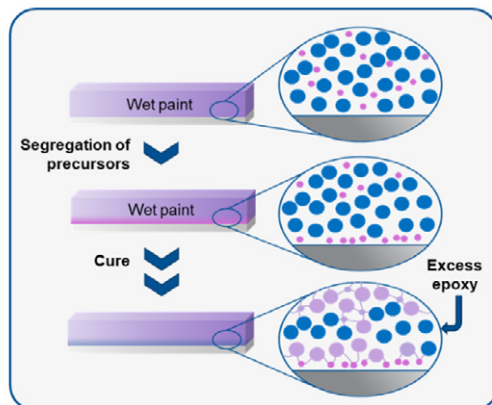
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Network-forming polymers are widely used in advanced composites, structural adhesives, protective paints and coatings. In all of these applications, interactions with inorganic surfaces (the oxide layer of metal substrates, pigments and fillers) occur both during and following step growth polymerization. Furthermore, the adsorption and segregation of the molecular polymer components are widely considered to yield extensive under-cured interphase regions, with distinct physical and chemical properties, that have been linked to key performance indicators such as adhesion, fracture toughness and small molecule transport. Historically however, this microscale interphase model has primarily been based on infrared spectroscopy of ultrathin films, and, in the case of epoxy-amine resins, the validity of these thin film models has recently been questioned. Contributions of amine carbamation and evaporation during sample preparation can increasingly retard the cure as the surface area to volume ratio increases. As a result, the extent and structure of interphase regions remains contentious. Central to this debate is the fact that the nanoscale buried interphase region remains inaccessible to conventional organic analysis techniques. Here, we will demonstrate the application of AFM-IR to directly interrogate chemistry of the interphase region in epoxies, generating new insights into the formation, chemistry and degradation of the buried interphase.



Day 2, Wednesday, September 7th

9:15 | Micro to Nano: a multi-scale IR spectroscopy studies of metal soaps in oil paints

*Xiao Ma*¹, *Georges Pavlidis*², *Georg Ramer*², *Victoria Beltran*³, *Mathieu Thoury*⁴, *Andrea Centrone*^{2, *}, and *Barbara H. Berrie*^{5, *}

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Oil paints comprise pigments, drying oils and additives that together confer desirable properties, but can react to form metal carboxylates (soaps) that may degrade the appearance and integrity of oil paints over time. In order to obtain information on soap formation and aggregation in oil paints, a multi-scale IR spectroscopic study was carried out on one commercial oil paint-out and one historic oil painting. The distribution of chemical phases including several types of different zinc carboxylates, oil film and other compounds in thin sections from those paintings were investigated at multiple scales (μ -FTIR $\approx 10^2 \mu\text{m}^3$, O-PTIR $\approx 10^{-1} \mu\text{m}^3$, PTIR $\approx 10^{-5} \mu\text{m}^3$). The IR techniques used provide chemical information over many length scales adding significantly to our knowledge of metal-carboxylate formation and distribution in paint. The synergy of the methods used here can be applied broadly to address issues that challenge art conservation and other fields where materials with multiscale chemical heterogeneity are important, such as biomedicine and energy storage.

9:45 | Vibrational spectroscopy at the nanoscale: from art history to high performance polymer blends

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² Department of Mechanical Engineering, Imperial College London, London, UK.

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A blend of Polybenzimidazole (PBI) and Polyetheretherketone (PEEK) has been investigated¹ for its potential use in several industries due to its high temperature stability and desirable tribological properties. Understanding the nanoscale structure and interfacial mixing of the two domains of the blend is critical for elucidating the origin of these desirable properties. In this talk, we combine Nano-IR Atomic Force Microscopy (AFM-IR) and thermal cantilever probes (nano-TA) to gain insights into the chemical heterogeneity and extent of mixing within the blend structure. The AFM-IR and nano-TA measurements show that domains in the blend are compositionally different from those of the pure PEEK and PBI polymers, indicating a likely physical mixing of the individual components at the molecular scale in the boundary region. In the light of the use of Nano-TA in the above, a deconstruction of the limitations of Nano-TA is presented showing the intrinsic limits of the technique. Further results are presented detailing an investigation into the morphology and chemistry of synthetic and natural blue pigments of relevance to the preservation of works of cultural importance, showcasing the application of Nano-IR as a non-destructive tool in conservation science. Finally recent advances in the application of tip enhanced spectroscopy to sum frequency generation are presented showcasing spatially resolved second order non-linear spectroscopy of mixed lipid monolayers.

1) *Polymers* (Basel). 2022 Jan 4;14(1):192. doi: 10.3390/polym14010192

10:15 | Application of Tapping-mode AFM-IR to a post-consumer waste Polyolefin recyclate

A. Catarina V. D. dos Santos¹, Davide Tranchida², Bernhard Lendl¹ and Georg Ramer^{1,}*

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The recycling of polyolefins remains a challenge. The need to sort polyolefin waste into its individual polymer types such as Polyethylene (PE) and Polypropylene (PP) to avoid undesired mechanical properties of the blends leads to increased recycling costs and decreased recycling rates. Therefore, recycled blends that retain the desired mechanical properties, but avoid the separation step of the recycling process be cost-advantageous. To understand the origin of a material's mechanical properties a look at its nanoscale constitution is indispensable. Currently, the standard techniques used to analyze the nanoscale (TEM, SEM, and AFM), provide no direct chemical information, and are thus dependent on a previous good knowledge of the polymer's composition which may not be available for complex heterogeneous samples such as recyclates. AFM-IR is a scanning probe technique that combines the resolution of AFM with the possibility to obtain IR spectra at the nanoscale with resolutions down to 10 nm. In this work, we apply tapping-mode AFM-IR to a commercially available polyolefin recyclate derived from post-consumer municipal waste. We were able to detect the presence of sub-micrometer sized polyamide and polyurethane impurities, as well as PP inclusions within the PE phase. Furthermore, the interface between the PP and PE phase was found to be composed of rubber present in the waste. The rubber distribution could be imaged with the help of a gaussian mixture model, and its location is in agreement with reference TEM measurements. The obtained results thus showcase the potential of AFM-IR in a recycled polymer characterization context.

11:00 | Detecting evolution and properties of bitumen surface microstructures at different environmental conditions: AFM-IR and NanoTA

Farrokh Tarpoudi Baheri^{1,2}, Thomas M. Schutzius³, Dimos Poulidakos², Lily D. Poulidakos^{1,}*

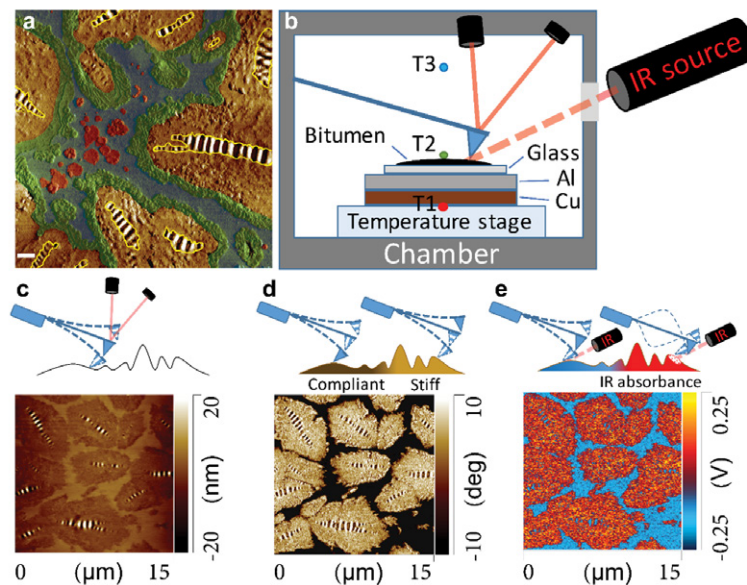
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One of the most widely used construction materials is bitumen. Which is used both directly and as component of composite materials in various applications ranging from road construction, paving, and roofing to sealing and gluing. It is known that bituminous surfaces can potentially develop surface microstructures. Advanced atomic force microscopy combined with infrared spectroscopy (AFM-IR) in an environmental chamber made it possible to demonstrate the chemistry and mechanical properties of bitumen surface with nanoscale precision for a broad temperature range. We showed that cooling bitumen to subzero temperatures can have several interesting effects on composition and texture of the three surface domains of: catana, peri, and para. At subzero temperatures, para domain significantly coarsens and develops sal-domain. We also showed that the peri and para domains are mechanically and chemically distinct at ambient conditions; however, when cooled to subzero conditions, phase imaging and nanoscale infrared spectroscopy indicate that the properties in sample domains appear to become similar and that the transition domain—which separates them—emerges and broadens. This can be expected on the one hand as the different domains go through their respective glass transition and display stiffer properties. The mechanical and chemical composition heterogeneity of domains lead to higher selective condensation and wettability on para domain. In the next step by conducting NanoTA analysis, the difference in thermal properties of bitumen surface microstructures was detected which can help to better distinguish effect of different modifications and additives on bulk bitumen properties.



11:30 | AFM-IR for nanoscale degradation assessment in industrial coil coatings

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Coil coatings are used to improve both the aesthetic properties and the durability of metallic materials exposed to aggressive environments. It has been widely used in e.g. roofing, facades, and rainwater systems for decades and is regarded as a mature technology. However, industrial research tends to focus on properties that are measured on the macro scale, such as gloss or color retention, even though local inhomogeneities have been shown to greatly effect the performance. Defects and inhomogeneities on the nanoscale can act as initiation points for damage and ultimately lead to and failure.

We will show examples of how AFM-IR can be utilized to evaluate local defects and inhomogeneities in coil coatings in various stages of degradation. This will be compared to IR-based micro and macro scale analysis techniques. Additionally, we will discuss the local effects of aggressive atmosphere on a metallic substrate material.

13:00 | Surface enhancement in AFM IR technique and its application in drug/metal nanocarrier characterization

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Surface – enhanced Raman (SERS) and surface – enhanced infrared (SEIRA) spectroscopies have become excellent tools for providing a detailed elucidation of the molecular spatial orientation on the metal nanosurface. Such interpretation is possible due to the developed surface selection rules,^{1,2} which explain how the spectral signals change before and after the adsorption of the molecule on the metal. In recent years, our studies tend to explain if the atomic force microscopy in combination with infrared spectroscopy (AFM – IR) ensures information about drug behavior on the metal nanoparticles. In this study, the application of AFM

– IR in the characterization of the adsorption process of the selected drugs (approved in non-small cell lung cancer therapy) on the metal nanoparticles' mono-layers will be discussed. Figure 1 presents the experimental scheme together with the AFM topography of the silver nanoparticle mono-layer after the erlotinib drug adsorption and the AFM-IR intensity map illustrating the spectral signal distribution of the characteristic drug band [$\nu(\text{CC})\text{Phe}$]. The performed investigations manifest the huge AFM – IR signal reinforcement on the silver nanosurface, which provides the spectral data recording even for a single mono-layer of drug adsorbs on the metal monolayer. Additionally, the well-known surface selection rules used in SEIRA technique proved their usefulness for the interpretation of the AFM – IR signal for the drug alone and after its adsorption on the metal mono-layer.^{3,4,5} These studies reveal the AFM – IR utility in the characterization of drug/metal interaction in the ultra-high spatial resolution, which allows for the opening of new directions of analysis.

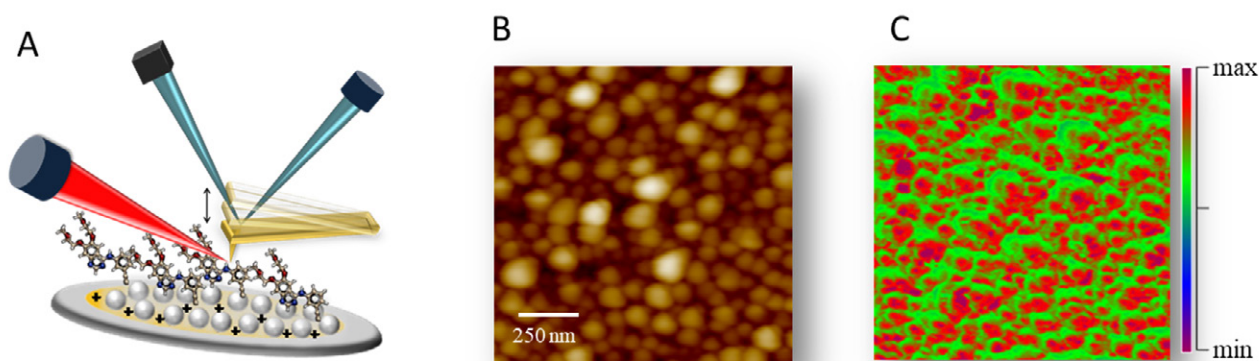


Figure 1. The experimental scheme of the AFM – IR measurements for erlotinib adsorbed on the silver nanoparticle mono-layer (A) together with the AFM topography of this nanosystem (B) and the AFM – IR intensity map of 1570 cm⁻¹ [$\nu(\text{CC})\text{Phe}$] band of erlotinib (C). The AFM – IR map proves the presence of the drug on the metal nanosurface.

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Acknowledgments

This work was supported by the National Science Centre Poland (No. 2016/21/D/ST4/02178 to N. P.). N. P. gratefully acknowledges the financial support of the French Government and the French Embassy in Poland. Some part of these measurements were also supported by the Paris Ile-de-France Region–DIM Matériaux anciens et patrimoniaux. The measurements were partly performed using the equipment purchased in the frame of the project co-funded by the Małopolska Regional Operational Program Measure 5.1 Krakow Metropolitan Areas an important hub of the European Research Area for 2007–2013, project no. MRPO.05.01.00-12-013/15e.

13:30 | From prism to flat silicon: Novel approach for AFM-IR measurements in liquids

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AFM-IR is a hybrid technique combining atomic force microscopy and mid-infrared spectroscopy. Pulses of a tuned EC-QCL source cause local short-lived photo thermal expansion, which excites the resonant oscillation of the AFM cantilever in contact with the sample. The oscillation amplitude is directly proportional to the absorption and an absorption spectrum is generated [1]. It is possible to perform experiments in liquid. However, this requires a bottom illuminated setup. IR Measurements in liquids (e.g., water) suffer from high absorption, thus conventional measurements require an IR transparent prism (e.g. ZnSe) on which the sample sits. Here, the ingoing undergoes a total internal reflection and the developed evanescent field on the crystal face interacts with the sample. Nevertheless, using a ZnSe prism comes with drawbacks, like not being suitable for every type of sample, difficulty of handling and sample preparation, functionalization of ZnSe is not trivial and there is little literature to this, also the cost of an ATR prism is not insignificant. We introduce a novel sample carrier for liquid AFM measurements on a flat, silicon ATR crystal. This opens up new ways for measuring AFM-IR in liquids. The flat shape allows easy handling and spin coating of samples on the carrier. Because it's made of silicon, surface functionalization is very easy, and one can refer to a lot of literature. We have shown that our new sample carrier allows cost-effective, functionalizeable measurements on the nanoscale in liquids.

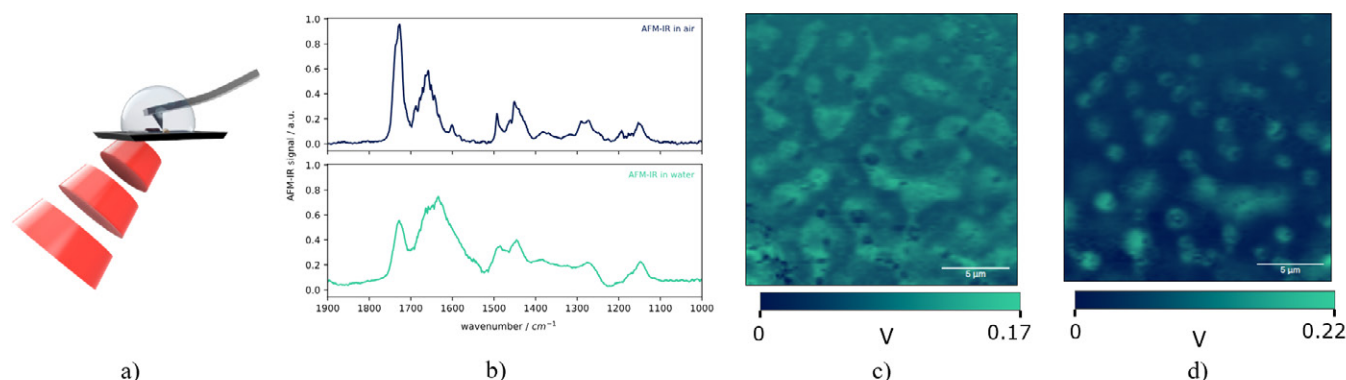


Figure 1: a) novel, flat Si-sample carrier; b) spectra taken on PMMA/PVP blend in air & liquid; c) IR imaging at 1732 cm^{-1} and d) IR imaging at 1660 cm^{-1} .

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13:45 | Infrared polarimetry to study the anisotropy of polymer nanofibers

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A straightforward multi-scale infrared (IR) spectroscopic characterization of anisotropy and arrangement of polymer nanofibers is presented [1]. Such fibers are of high technological relevance in optoelectronic, bio-related and medical applications (see Refs in [1,2]). Functionalization, anisotropy and ordering are characteristic nanofiber properties. We investigate fiber bundles and single fibers via direct spectral interpretation with respect to their anisotropic properties. This is possible by applying non-invasive IR polarimetry at defined polarization states with spatial resolutions from the macroscale (a few mm) down to the

nanoscale (a few 10 nm). A direct relation of vibrational absorption bands in s-polarized reflection spectra and s-polarized photothermal AFM-IR spectra between 1000 cm^{-1} and 1770 cm^{-1} is shown. The direction of specific transition dipole moments is discussed. The rotation of a single fiber allows for the differentiation of isotropic and anisotropic contributions. For both techniques the use of s-polarization ensures that only related in-plane absorption properties are detected. Future polarimetric possibilities using dual-comb polarimetry for the study of nanofiber scaffolds are touched upon briefly.

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14:15 | Towards a point spread function for nanoscale chemical imaging

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Atomic force microscopy-infrared (AFM-IR) is an AFM based technique that measures mid-IR absorption spectra at nanometer spatial resolution. The technique of AFM-IR relies on the detection of the pulsed wavelength tunable IR laser induced thermal expansion of the sample area underneath the AFM tip. In this work, we present a theoretical investigation of the laser heating induced thermal expansion process and model it as a point spread function (PSF). This approach draws parallels to super resolution microscopy where the PSF is used to determine spatial resolution and to resolve features below the diffraction limit. By solving the inhomogeneous heat equation with a volumetric heat source, we obtain the PSF of AFM-IR in frequency domain displayed as surface displacement which in dependence of laser heating. To verify that simplified boundary conditions do not result in a significantly changed behavior a finite element model of heat conduction in solids and fluids (implemented in COMSOL Multiphysics 5.6) of more realistic sample geometries is used. In the experimental part, we prepared $1\text{ }\mu\text{m}$ thick samples by mixing polyethylene and PMMA beads with a diameter of about 140 nm . First results show that there is a frequency (pulse repetition rate) and pulse length dependence of the PSF in AFM-IR. The achievable spatial resolution is improved for short pulses and high frequencies. These results provide guidance for experimental parameters which can be considered as trade-off between spatial resolution and signal intensity.

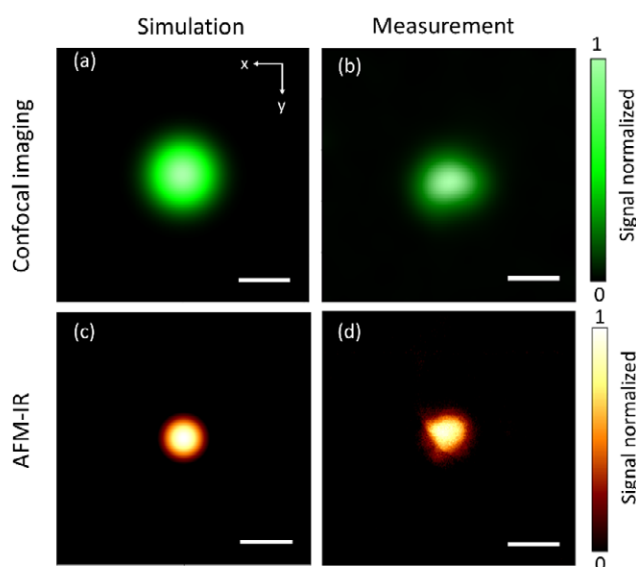


Figure 1. Comparison of simulated PSF imaging with experimental imaging. (a) Simulated PSF of confocal imaging at N.A. 0.9 and 540 nm emission wavelength. (b) Measured confocal fluorescence imaging of single PMMA bead. (c) Simulated 140 nm diameter size absorber in the center of the sample based on PSF of AFM-IR with 100 ns laser pulse width and 280 kHz repetition rate. (d) Measured AFM-IR chemical imaging at wavenumber 1730 cm^{-1} .

14:30 | Advanced probing of light-matter interaction at nanoscale for quantum optoelectronics

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Within the Quantum Materials & Sensors group at NPL, we focus on the physics, engineering and metrology of quantum and non-quantum materials and related devices for emerging quantum technologies, underpinning both fundamental research in academia and relevant R&D in industry. In particular, I will showcase some of our most recent development in our nano-optical capabilities for characterising a wide range of materials and devices for potential quantum optoelectronic applications using the nanoIR2-s system. As examples, I will show in this talk how we have developed our s-SNOM based capabilities to: (i) characterise dielectric properties and nanoscale IR response of h-BN/graphene heterostructures and topological insulator nanostructures; (ii) enable sub-diffraction imaging of polaritons in vdW materials; (iii) perform nanoscale imaging of waveguide modes in metamaterials towards broadband mid-IR SPDC applications (listen to our other talk for more details); (vi) extend the range of detectable material properties of by adding electrical readout to establish mid-IR and visible near-field photocurrent nanoscopy. I will also show how our AFM-IR capabilities help the industry on materials validation such as chemical analysis of surface features and contaminants for quality control and process engineering, as well as providing nanoscale optical metrology for biosensors based on functionalised quantum materials. We are continuing developing and establishing new capabilities towards a diversified suite of nanoscale correlative and hyperspectral optoelectronic characterisation capabilities which will be immensely valuable to our stakeholders in R&D and commercialisation of quantum materials and a new generation of quantum optoelectronics that will disrupt many quantum-enabled industries and sectors such as ICT, healthcare, energy & environment.

15:30 | Exploiting infrared light-matter interaction for deterministic and tunable nanomachining of 2D materials

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Tailoring two-dimensional (2D) materials functionalities to applications in optoelectronics, catalysis, and quantum computing closely intertwines with defect engineering. Defect formation is environment-dependent and affects the material properties around the defect site. However, conventional methods do not offer the necessary control to locally introduce and study defects in 2D materials in non-vacuum environments. Here, we demonstrate that an infrared pulsed laser focused at the tip of a metallic atomic force microscope cantilever can be used to create nanoscale defects in hexagonal boron nitride (h-BN). We also show that the lattice distortions during and after the defect creation event by means of nanoscale infrared (nanoIR) spectroscopy. With this approach, we evaluate the effect of incoming light power, exposure time and environmental conditions on defected regions formed at the tip-sample interface. The measurements reveal changes in lattice vibrations discriminating defects with different morphologies formed under various environments. In summary, we illustrate how this new nanomachining approach can be used to tailor the properties of 2D materials via deterministic engineering of defects for a broad range of applications.

16:00 | s-SNOM as an interrogation technique of optical modes of plasmonic metamaterials for novel applications in SPDC in the mid-IR

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Spontaneous parametric down-conversion (SPDC) optical process lies at the heart of several applications in quantum technologies, such as quantum imaging and communications. The low down-conversion emission rates, and limited operation frequencies of currently available non-linear crystals for SPDC, lead to constraints in device designs and integration. As alternative sources, the specific design of plasmonic metamaterials can enable resonant and non-resonant, broadband, non-linear down-conversion sources with enhanced Purcell factor. The accurate characterisation of the locally induced optical resonances in such systems, which is of paramount importance in assessing the performance of the metamaterial, can be achieved by implementing s-SNOM. In this talk, I will discuss general concepts in the motivation, design by optimised numerical simulations, and fabrication of a plasmonic metamaterial structure, based on a composed nanoantenna/waveguide array, for applications as SPDC sources in the mid-IR. We present preliminary results on the local optical properties of such metamaterials, measured with a cross-polarised s-SNOM technique at different frequencies in the mid-IR range, and with different angles of incidence. Such results highlight the effectiveness of s-SNOM technique for the characterisation of the resonant waveguided optical modes in metamaterials, in particular, cross-polarised s-SNOM for investigating the coupling between far-field excitation and near-field signal of tailored metamaterial nanostructure orientations. Further discussion on potential improvements of this technique will also be addressed.

16:15 | Study of steaming effects of ZSM-5 zeolite using AFM-IR technique

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Micro-spectroscopic techniques (micro-IR, micro-Raman) are not capable to distinguish differences in crystal structure smaller than several micrometers [1]. In our work, we studied intra- and inter-crystals heterogeneity of ZSM-5 zeolites (Si/Al = 22, 25; 10 nm – 3 μm) using atomic force microscopy coupled with infrared spectroscopy (AFM-IR). Local analysis on the surface of zeolite crystal (Fig. 1) showed that different contributions are present below the maxima at ca. 1106 cm⁻¹. This band changes its position by 21 cm⁻¹ to the region of lower wavenumbers along the analyzed line. It can be due to increasing Al content on the right side of the crystal. Band at 1219 cm⁻¹ that represents inter-tetrahedral asymmetric stretching framework vibration showed less sensitivity to the chemical composition than the intra-mode [3]. However, the ratio of band intensities (I1/I2) decreases almost by 5 times which means a decrease in the long-range order. The concentration of surface defects [4] is higher on the right edge of the agglomerate. These spectroscopic features could be at the origins of specific surface reactivity and are of interest from a catalytic point of view and / or zeolite crystal design / modification.

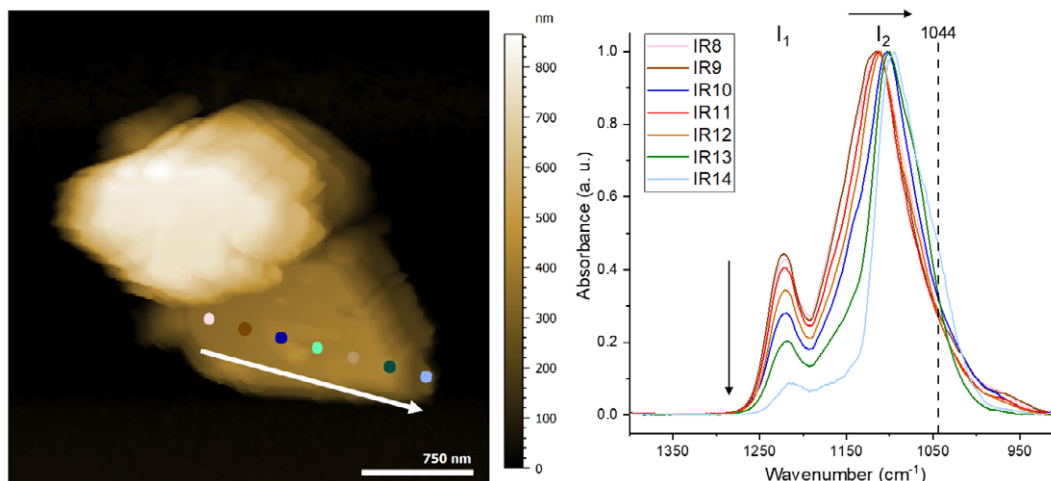


Fig. 1. Left: Topography AFM image of Z-22calc sample agglomerates; right: comparison of AFM-IR spectra

References:

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- [2] D. Kurouski, A. Dazzi, R. Zenobi, A. Centrone, Infrared and Raman chemical imaging and spectroscopy at the nanoscale, *Chemical Society Reviews*, Vol 49, 3315-3347 (2020).
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- [4] B. Mihailova, V. Engström, J. Hedlund, A. Holmgren, J. Sterte, A vibrational spectroscopic study of the growth of silicalite-1 films on seeded gold surfaces, in *Porous materials in environmentally friendly processes*, Proceedings of the 1st international FEZA conference. Elsevier, 221-228 (1999).

16:30 | Tiny Data: Nanoscale hyperspectral imaging

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AFM-IR gives access to infrared absorption information at nanoscale lateral resolution. For chemically simple samples (few components, distinct phases, spectroscopically different samples) ratio images and direct evaluation of spectra can often be sufficient to understand chemical composition. When these approaches fail for more complex samples (spectroscopic overlap of components, many components, inter-diffusion) multi-variate methods can be applied to gain deeper insights. Multi-variate methods enable to combine information from multiple spectra or multiple single wavelength images into actual maps of chemical composition – if we are doing it right. “Doing it right” requires an understanding of the signal transduction chain in AFM-IR and the peculiarities of scanning probe microscopy. It also requires to understand optical effects that limit the linear range of AFM-IR [1]. This presentation will discuss the AFM-IR signal transduction chain and which of its parameters can (need to be) controlled to achieve reproducible AFM-IR measurements and what the challenges are in applying chemometric algorithms to AFM-IR datasets. It will also introduce software packages that enable hyperspectral AFM-IR imaging and machine learning.

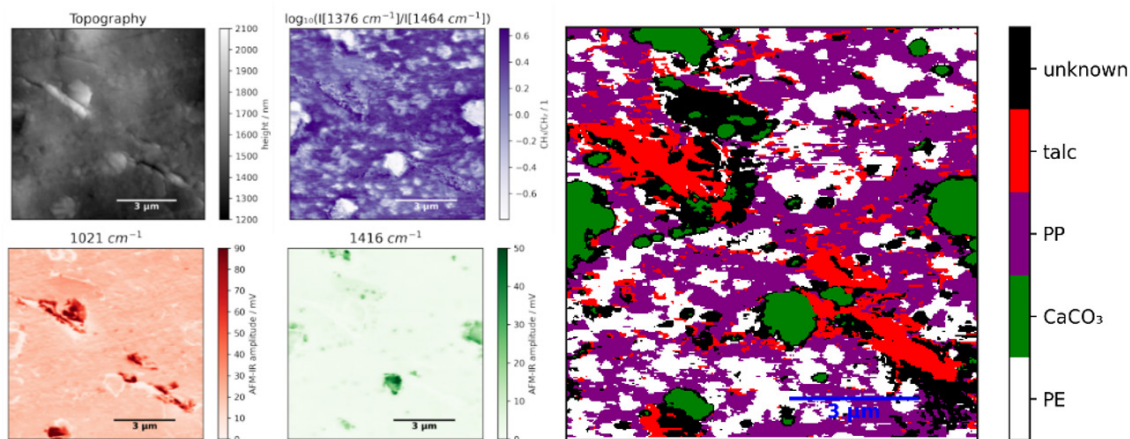


Figure 1: Left: Topography and single wavelength images of a polymer material. Right: Chemical image calculated via Gaussian unmixing (reproduced from [2]).

[1] G. Ramer, V. A. Aksyuk, and A. Centrone, *Anal. Chem.*, vol. 89, no. 24, pp. 13524–13531, Nov. 2017, doi: 10.1021/acs.analchem.7b03878.

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Poster Abstracts

1 - Electrical transport dynamics of conducting polymers under nanoconfinement

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The electrical transport of conducting polymers such as poly(3,4-ethylene dioxythiophene): poly(styrenesulfonate) PEDOT:PSS have shown significant enhancement in conductivity when confined in an array of nanochannels in form of alumina nanopillars.(1) The transverse conductivity along the nanopillar axis, which is an otherwise suppressed quantity, increases nonlinearly by 3-4 orders in magnitude as the diameter of the scaffold-pore is decreased to 20 nm, when measured at single nanochannel level as well as at bulk-macroscopic level, suggesting the major role of dimensions and geometry in eliciting efficient electrical transport. Similarly, more than 3 orders of conductivity increase have been shown by in-situ polymerized poly(3,4-ethylenedioxythiophene):tosylate, PEDOT:Tos within the nanochannels. Non-zero dc conductivity at T 0, improved order-parameter in the existing disordered PEDOT matrix within the nanochannels have indicated enhanced transport characteristics.(2) The rearrangement of interconnected microstructures of various forms of PEDOT under confinement opens up scope to tune the electrical and thermal properties. We utilize the property of PEDOT:PSS as a hole transporting layer and investigate photodetection properties of a hybrid organic-inorganic perovskite photodiode. Hole extraction in a nanoconfined device is efficient as compared to bulk devices. The results showing higher responsivity and faster response times in PEDOT nanochannel devices will be discussed.

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(2) Sukanya Das, Anil Kumar, K.S. Narayan, Confinement Highlights the Different Electrical Transport Mechanisms Prevailing in Conducting Polymers, *Phys. Rev. Materials* 6, 025602, (2022).

2 - Towards in situ and in vitro AFM-IR studies of neurodegenerative disease

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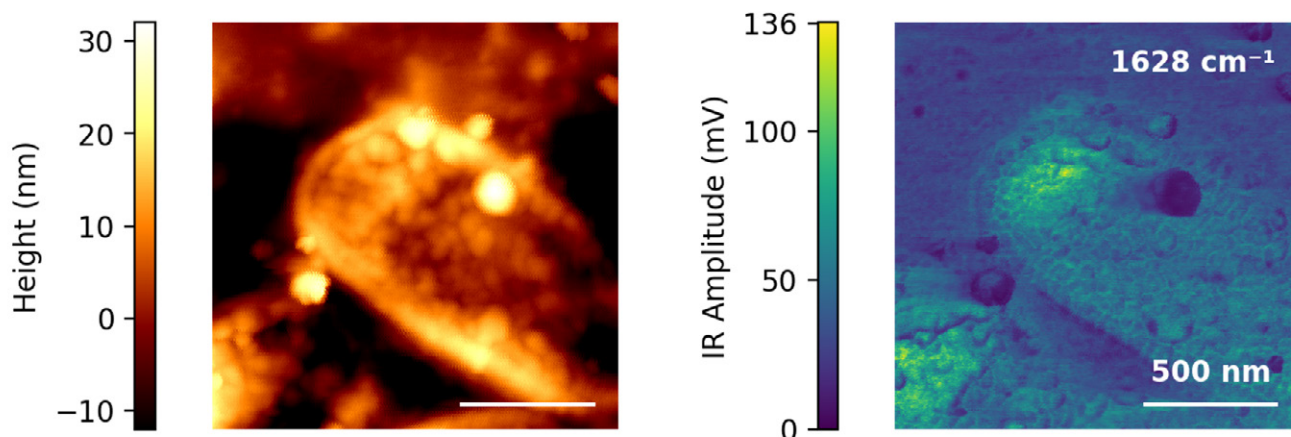
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Many neurodegenerative and related diseases feature misfolding and aggregation of proteins into amyloid fibrils, a multimeric structure rich in intermolecular beta sheets. Some proteins can form several classes of fibrils that differ in their secondary structure and this polymorphism may, at least partially, correlate with the pathological variability of the diseases they are implicated in. Using infrared nanospectroscopy (AFM-IR), we aim to characterize the structural diversity of amyloid fibrils in situ and in vitro, and the environmental conditions that may determine it. As a test case for patient tissue sampling, we exposed *E. coli* bacteria to several stressors (chemical, physical and biological) and embedded them in an epoxy resin (see figure). We

have shown that AFM-IR can distinguish between protein aggregates generated by these different stressors. We have also deposited fibrils consisting of Tau and amyloid- β , which play a major role in Alzheimer's Disease, on gold substrates to collect single-fibril spectra. However, we have not yet managed to reliably acquire IR spectra or spectral images from these samples. With this research, we hope to learn more about the interaction between protein structure and pathology for a wide class of diseases.



Inclusion bodies (protein aggregates on a scale of ~ 100 nm) are visible on both topography maps (left) and spectral images around 1620 - 1630 cm^{-1} (right).

3 - Applications of AFM-IR in polymer industry

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Since 2014, the Analytical Science department of ExxonMobil, Brussels, Belgium, has been equipped with AFM-IR system nanoIR1. The possibility to have localized IR spectra and localized softening point measurements, combined with the high resolution of the instrument, are key factors to characterize and study challenging polymeric samples at a nanoscale level. The development of this capability allowed us to remain up to date with the developments and challenges of the polymer industry. Some examples are given in this poster.

Highlighted applications concern 1) structural identification of blends as ICP (Impact CoPolymer), 2) multilayer determination, 3) interphase characterization, 4) delamination issues study, 5) Biodegradable polymer characterization, in 5) combination with thermal analyses.

4 - Direct visualization of the drug loading of single DNA Origami nanostructures by AFM-IR nanospectroscopy

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Over the last decade, the relevance of DNA origami nanostructure [1] in biophysics and biomedicine [2] drastically increased, in particular with regard to applications in drug delivery. For this, efficient loading of DNA nanostructures with intercalating or groove-binding drugs is required. However, unambiguous verification and quantification of successful drug loading is often rather challenging. In this work [3], AFM-IR nanospectroscopy is thus employed to directly visualize the loading of DNA origami nanostructures with the

photosensitizer methylene blue (MB). Single MB-loaded DNA origami nanostructures can be clearly resolved in high-resolution infrared (IR) spectra and the occurrence of MB-specific IR absorption correlates well with the topographic signals of the DNA origami nanostructures (see. Figure 1). Furthermore, a correlation between the used concentration of MB and the detected intensity could be directly shown in the MB absorption bands. Finally, investigation of different MB-loaded DNA origami nanostructures, i.e. triangles, six-helix-bundles and 24-helix-bundles, revealed a correlation of the IR-signal with the thickness of the individual shapes.

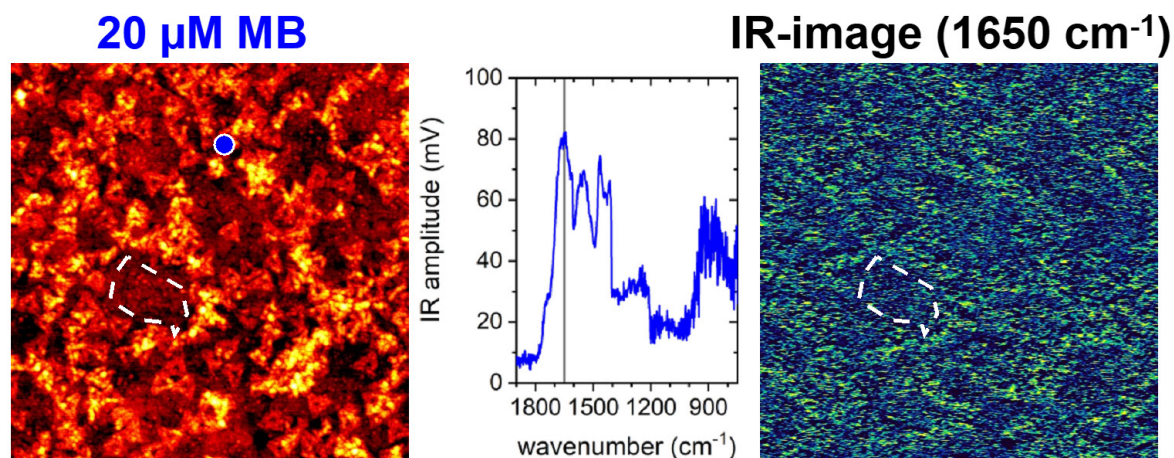


Figure 1. Topographic AFM image (left), IR spectrum (center), and corresponding IR map (right) of MB-loaded DNA origami triangles adsorbed on template-stripped gold surfaces.

[1] P.W. Rothmund (2006). *Nature*, 440, 297–302.

[2] S. Dey et al. (2021). *Nature Reviews Methods Primers*. 1, 13.

[3] M. Hanke et al. (2022). Under revision.

5 - Chemical spectroscopy of individual human milk extracellular vesicles

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Extracellular vesicles (EVs) are nanosized particles, which are associated with various physiological and pathological functions. They play a key role in intercell communication and are used as transport vehicles for various cell components. In human milk EVs are believed to be important for the nutrition of infants and for the development of their acquired immunity. State of the art analysis methods are not able to provide label free chemical information at the single vesicle level, hence new analysis techniques are required to study the chemical difference withing EV (sub-)population [1]. We introduce a protocol to profile structure and composition of individual EVs with the help of photothermal scanning probe infrared spectroscopy (AFM-IR). First, EVs are immobilized onto a silicone surface using microcontact printed Anti-CD9 antibodies. AFM-IR then provides both EV size and mid-infrared spectra for individual vesicles. The received spectra compare favorably to bulk reference spectra. In addition, AFM-IR images provide spectral information for multiple EVs within a single measurement. Stacking images taken at different wavenumbers yields hyperspectral chemical images of vesicles at nanoscale spatial resolution.

[1] K. Vaswani u. a., „A Method for the Isolation of Exosomes from Human and Bovine Milk“, *J. Nutr. Metab.*, Bd. 2019, S. 1–6, Dez. 2019.

6 - Photothermal AFM-IR unveils nanoscale features and chemical information of wood cell walls

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Wood cell wall have typical structures with the tight organization of cell wall polymers, which limits the swellability, solubility and reactivity of cellulose fibers during the production of value-added products, i.e. nanocellulose, bioethanol. Therefore, we applied electron microscopy and spectroscopy specially photothermal AFM-IR for analyzing the surface structures and chemical compositions of the wood cell walls. Therefore, this study contains different plant species to study the several exiting transition layer of wood cell wall for example, in spruce, transition layers S_{1-2} , S_1 -CML (compound middle lamella) and willow inner bark. In this study the electron tomography on ultrathin spruce and willow inner bark sections was applied to observe the three-dimensional (3D) structure of the transition layer(s). Surface characterization was measured by AFM-IR on wood sections, where the high-resolution images revealed 5–20 nm wide lignin-free areas in the cell wall layers.

The overall findings were seen in the way of structural differences, fibril orientation, surface characterization and its possible role in wood cell walls have been discussed. Photothermal AFM-IR, especially, are expected to bring new knowledge on nanoscale physical and chemical structures on wood cell wall as this nanoimaging technique of nanoIR (BRUKER) has never been applied for wood/pulp fibers.

7 - Detecting the influence of inter-particle proximity on the catalytic properties of NPs

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Molecular level understanding of catalytic processes provides crucial knowledge about reaction mechanisms which is essential for the development of highly-efficient and selective catalysts. However, heterogeneities in the size and composition of solid catalytic particles makes it difficult to directly monitor and identify the influence of various physiochemical parameters on the catalytic reactivity and selectivity. Thus, detailed chemical information at the nanoscale is required for understanding how surface properties direct the reactivity of catalytic particles, particularly at the single particle level. Surface properties can be mapped with high spatial resolution, and catalytic conversion can be tracked with a clear chemical signature. To study the size and composition contribution of adjacent NPs on their catalytic properties, pairs of dissimilar metallic NPs with varying inter-particle distance, were prepared and coated with (N-heterocyclic carbenes) NHCs as markers. IR nanospectroscopy measurements were conducted at the nanoscale and probe the inter-particle proximity influence on the hydrogenation (hydrogen spillover) process, and thus on the reactivity and selectivity of neighboring metallic NPs.

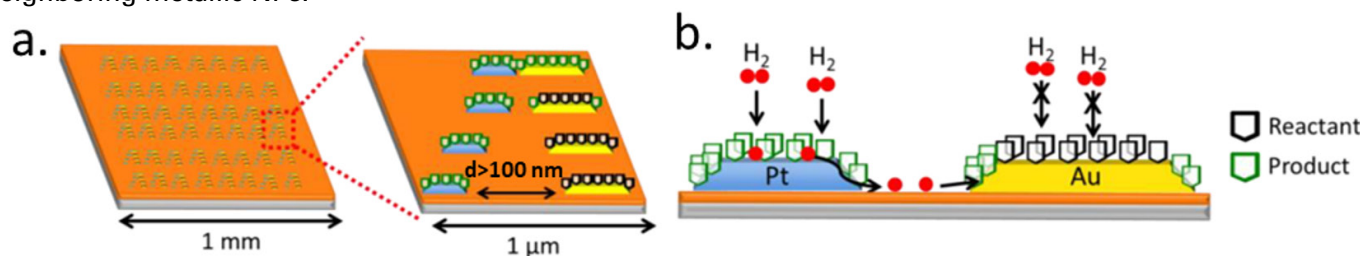


Figure 1. Schematic representation of model systems for detection of spillover effects by IR nanospectroscopy. a. Au and Pt NPs pairs with varying inter-particle distances prepared and coated with NHCs. b. Hydrogen spillover from Pt to Au NPs can activate catalytic reactions on the Au surface.

8 - Nanoscale characterization of single chiral polymer chains

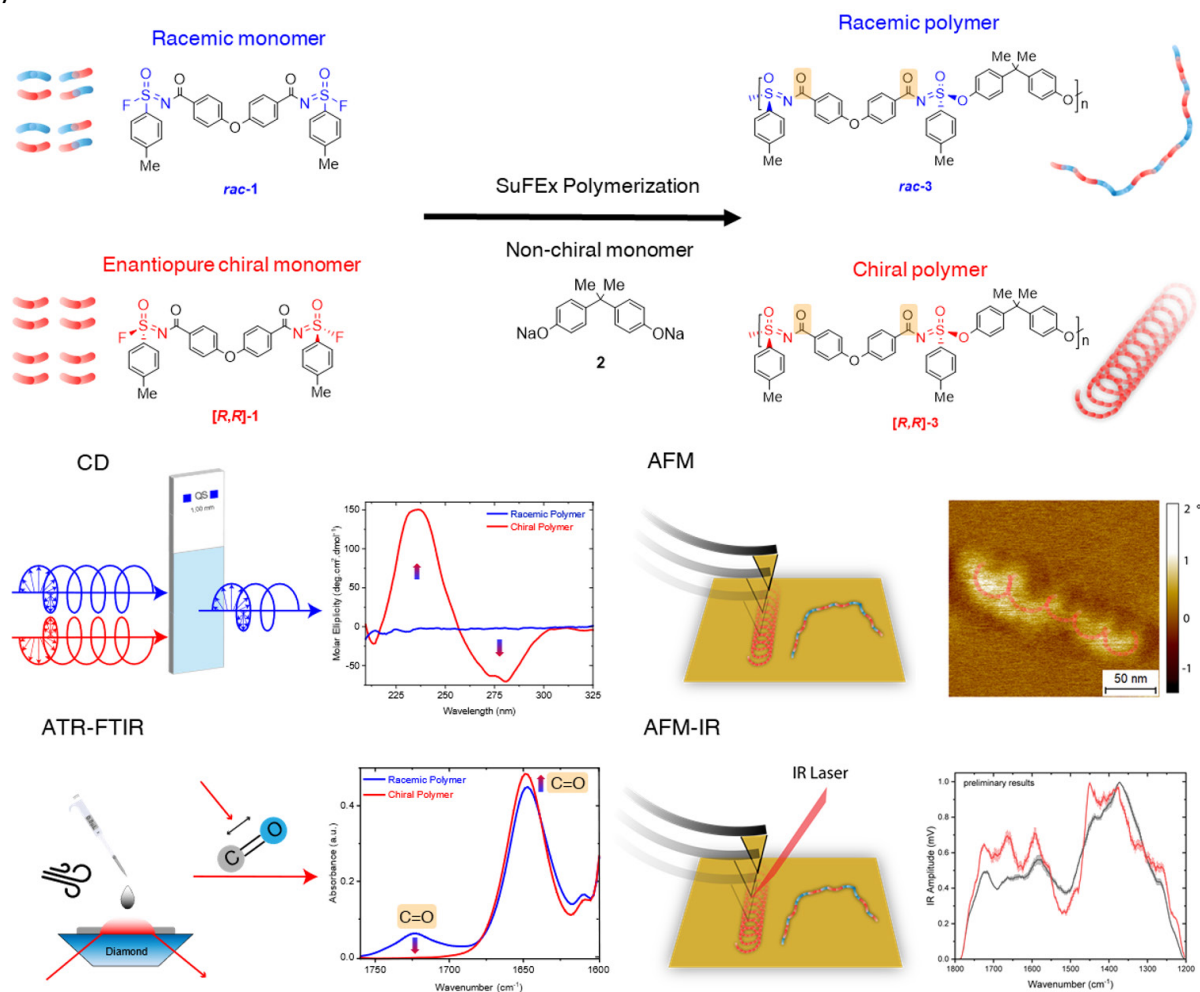
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Helical polymers are comprehensively studied in various research areas, e.g., molecular biology, polymer chemistry, material science, medicine and optics for their diverse functions involving recognition, catalysis and circular polarized luminance. Numerous spectroscopic and imaging methods have been developed to unravel the supramolecule chirality. However, how supramolecular chirality arises and differs from central chirality has not been thoroughly studied. The new click reaction based sulfur–fluorine exchange (SuFEx) polymerization enables green synthesis from the same chemical form with different central chirality to polymers with or without configurational backbone chirality. Here, we utilize multi-dimensional characterization methods, from micro scale by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and circular dichroism spectroscopy (CD) to nanoscale by atomic force microscopy (AFM) and atomic force microscopy-infrared spectroscopy (AFM-IR) to resolve the structures and differences between polymers and monomers. Our initial results demonstrate that the carbonyl groups in racemic polymer are partially split to a higher wavenumber compared to chiral polymers and racemic polymers are more prone to self-assemble compared to chiral polymers which could be attributed to difference in backbone chirality. Based on these findings, we would like to further investigate from bulk to single chains, from morphological to chemical, leveraging the single molecule morphological and chemical sensitivity of AFM-IR to resolve spectral differences caused by supramolecular chirality and polymorphisms to answer the question how supramolecular arise from central chirality.



9 - Nanochemical microscopy of polymer systems: limitations and peculiarities

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To elucidate a structure of polymeric materials, Fourier Transform Infrared (FTIR) spectroscopy is a well-known and reliable tool. Using FTIR spectroscopy, in most cases, one can characterize unambiguously chemical composition, crystallinity, orientation, intermolecular interactions and lateral distribution of different components in the investigated polymeric systems. Regarding imaging measurements, however, the so-called diffraction limit restricts FTIR strongly, especially in the case of FTIR microscopy in the range of several micrometers. Since 2005 a powerful combination of atomic force microscopy and IR spectroscopy (AFM-IR) was established, which solved the issue of diffraction limit obstacle, by providing nowadays measurements with lateral resolution down to tens of nanometers. Despite the excellent qualitative agreement between AFM-IR and FTIR spectra, there are some practical peculiarities in sample preparation, measurement and technique limitations, which are worth to be mentioned. The aim of this work was to highlight such difficulties in working with polymers and in understanding AFM-IR results, to avoid data misinterpretation in practical applications. Research materials were an amide-ether copolymer, a semi-aromatic polyamide and poly(olefine-urethane) blends, because of the good spectroscopic contrast of the different components. Prior to the measurements, the samples were microtomed at different thicknesses (0.3 – 20 µm). The AFM-IR system NanoIR2 (Anasys-Bruker) coupled with an OPO-laser was used to acquire AFM-IR spectra and images of the samples. The limitations in sample preparation, and the qualitative and quantitative differences and peculiarities between conventional FTIR and AFM-IR spectra, and the influence of the IR-source on the results and spectra interpretation will be discussed in detail.

10 - Multicomponent covalent chemical patterning of Graphene: AFM-IR for chemical characterization of nanometer-thick layers of functional groups

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The chemical patterning of graphene is being pursued tenaciously due to exciting possibilities in electronics, catalysis, sensing and photonics. Despite the intense efforts, spatially controlled, multifunctional covalent patterning of graphene has not been achieved. The lack of control originates from the inherently poor reactivity of the basal plane of graphene which necessitates the use of harsh chemistries. Here we demonstrate spatially resolved multicomponent covalent chemical patterning of single layer graphene using a facile and

efficient method. Three different functional groups could be covalently attached to the basal plane in dense, well-defined micrometer wide patterns using a combination of lithography and a self-limiting variant of diazonium chemistry requiring no need for graphene activation. The layer thickness of the covalent films could be controlled down to 1 nm. I will discuss the application of nanoscale AFM-IR for the characterization such ultrathin layers of organic functional groups covalently bound to the graphene surface together with challenges encountered in the characterization.¹

References:

1. ACS Nano 2021, 15, 10618–10627.

11 - Too small to succeed: Why enhanced resonance AFM-IR cannot easily detect nano-objects

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Emergence of quantum cascade laser (QCL) in the AFM-IR field has been one of the major breakthroughs for the technique. The capacity of QCL to tune its pulse rate from 1 kHz to 3 MHz is a key factor for resonance-enhanced AFM-IR mode (Lu et al. Opt Express). In RE-AFM-IR, the pulse rate is selected to match one of the contact resonances of the cantilever which lead to move from a damped oscillation observed in classic AFM-IR to a “forced” one. This mode dramatically increases the sensitivity of the technique. Analytical description of the RE-AFM-IR demonstrates that the increase in sensitivity, compared to the classical way, is proportional to the Q-factor of the chosen contact resonance. Theoretically, this Q-factor amplification should be enough to study samples as small as self-assembly monolayer. However, in practice, these measurements are impossible without gold coated tip which generates a rod effect leading to a huge local field amplification to compensate weak sensitivity. To understand the contradiction between the theory and the experience, we have investigated the thermal behavior of smallest objects under a train of pulses to simulate the QCL illumination using a finite element simulation (COMSOL). The obtained results clearly highlight a change of the thermal expansion of objects of size below 25 nm of thickness which was not considered before. These numerical calculations are in good agreement with measurements realized on type I collagen with different thicknesses. These results allow us to propose an updated cantilever motion equation of RE-AFM-IR mode for small objects analysis.

12 - AFM-IR analysis in human breast tissue to decipher breast microcalcifications genesis and potential link with cancer

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Breast microcalcifications (BMCs) refer to calcifications between a dozen microns up to one mm within the breast tissue. As of now, only a few studies have investigated the chemical composition of BMCs with respect to the pathology; but two of them emphasize that the carbonate and magnesium content of BMCs might be correlated with decreasing and increasing risks of malignancy respectively [1,2]. Yet, the possible correlation between BMCs' chemical speciation and the pathology remains unclear, and the breast mineralization processes are still poorly understood. Therefore, we established a multiscale approach based on electron microscopy and infrared micro and nano-spectromicroscopy to specify the morphology and chemical composition of BMCs in their native environments. Using AFM-IR, we characterize nanometric BMCs and the

internal structure of micrometric BMCs directly in breast biopsies (Figure 1). Thanks to AFM-IR, we describe for the first time the internal heterogeneous structure of BMCs (Figure 1B and 1C) and highlight the presence of different phases of calcium phosphate within a single BMC; including amorphous carbonated calcium phosphate and whitlockite, while the current classification distinguishes only two types of BMCs: type I made of calcium oxalate dihydrate and type II made of calcium phosphate apatite. As BMCs' chemical composition reflects the environment in which they developed, such chemical nano-speciation is essential to depict mineralization processes in the breast. In addition, these results emphasize that AFM-IR is a promising tool for the physicochemical analysis of complex chemically and mechanically heterogeneous biological samples such as human tissues [3].

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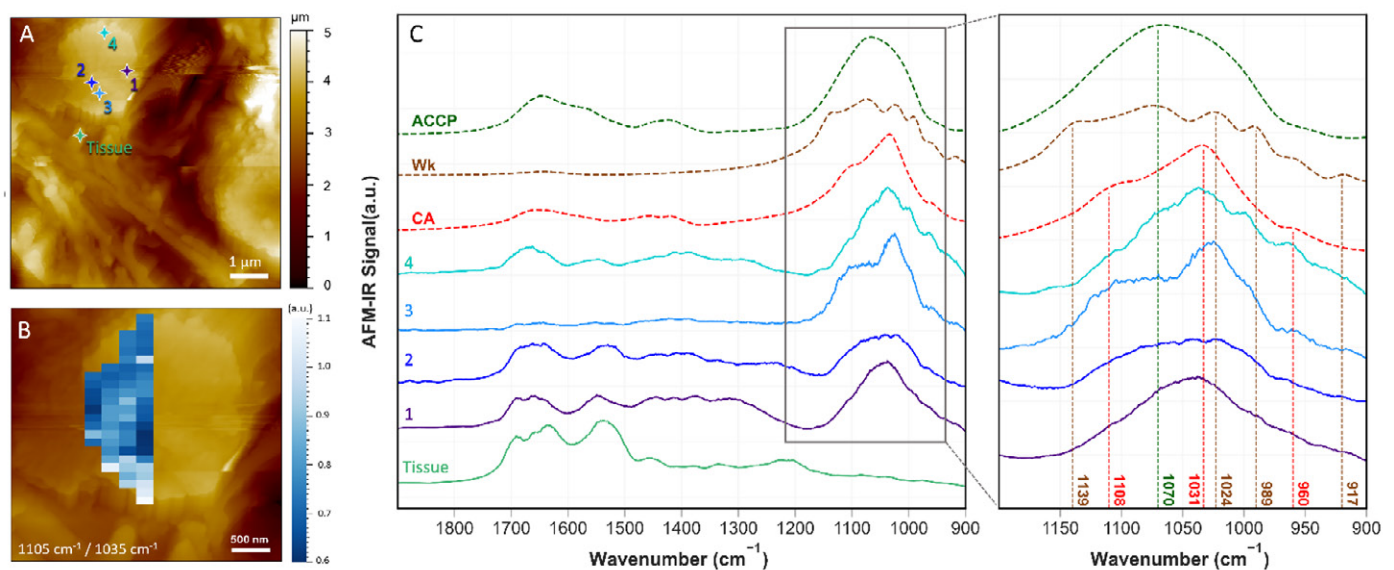


Figure 1 – AFM-IR analysis of a breast biopsy with microcalcifications from a 75-years old patient diagnosed with invasive ductal carcinoma. A) AFM topography of a microcalcification surrounded by tissue. B) AFM-IR topography zoomed on the calcification and hyperspectral analysis: ratio of the absorption signal at $1105\text{ cm}^{-1}/1035\text{ cm}^{-1}$ (variation of the BMC phosphate band). C) AFM-IR local spectra (solid lines) measured within the calcification and in the tissue as indicated by the color-coded crosses on A). Dashed lines are FT-IR reference spectra of amorphous carbonated calcium phosphate (ACCP), whitlockite (Wk), and carbonated calcium phosphate apatite (CA).

13 - New insight of Orgueil C11 chondrites using nano-IR spectroscopy

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The Orgueil meteorite fell near Montauban, France on May 14, 1864. It has been classified in the CI1 group of carbonaceous chondrites (C-type), and it is one of the most studied meteorites. After a few weeks of its fall, numerous analyses performed at the Paris Museum reported the presence of carbon-rich compounds, iron sulfides, phyllosilicates, carbonates, and soluble salts including ammonium salts and sulfates which were observed to be remobilized at the surface of the sample¹. Recently, we have been able to analyze a sample of Orgueil conserved in the sealed flask (Orgueil Flask). This sample may be relatively “fresh” compared to others more exposed to air and humidity, such as the one obtained by the Museum of Montauban (Orgueil Museum). In addition, we have also analyzed samples returned from the asteroid Ryugu (C-type) by the Japan Aerospace Exploration Agency (JAXA), which are thought to be similar in composition to CI chondrites². The “bulk” Ryugu samples also show some spectral reflectance bands corresponding to the NH-rich compounds³. Altogether, we aim to characterize two samples: “Orgueil Museum” and “Orgueil Flask”; based on sub-micron scale spectroscopy (e.g., AFM-IR) to understand better not only the N-bearing molecule but also the mineralogical and organic structure. Two laser sources were used to identify the chemical imaging and local IR spectrum in the two different spectral ranges: the APE laser and the Firefly laser for the 2000 – 700 cm⁻¹ and the 4000 – 2700 cm⁻¹ wavenumber, respectively. We will be present at the conference with the data set obtained so far.

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14 - AFM-IR studies of cysteine adsorption behavior on the Au nanoparticles-titanium surfaces

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One of the effective ways for improving the corrosion resistance is the surface modification of the material by using inhibitors, for example, organic molecules. Cysteine, the sulphur-containing compound, is the fundamental amino acid, which has shown an inhibition effect in the corrosion process of different metallic surfaces [1]. Gold nanoparticles (AuNPs) are broadly used for different nanomedical applications and the incorporation of NPs on the materials used in implantology can be a good way to improve the antibacterial [2] as well as corrosion properties [3]. In our research, AuNPs were deposited onto pure Ti using a magnetron sputtering combined with the Inert Gas Condensation technique. The adsorption process of cysteine on the modified metallic surface was investigated under simulated inflammatory conditions (i.e., T= 37°C and pH=5) in simulated body fluids (PBS solution-phosphate buffer saline) after 24 h of immersion time, with and without the addition of different cysteine concentrations (10⁻³ M and 10⁻⁵ M). Surface-enhanced infrared absorption spectroscopy (SEIRA), surface-enhanced Raman spectroscopy (SERS), and a technique that combined conventional IR with atomic force microscopy (AFM-IR) were employed to study and assess the adsorption process. Figure 1 presents the AFM topography of the exposed AuNPs-Ti surface in presence of cysteine with height profiles (the size of NPs on the Ti surface up to 10 nm) and the AFM-IR intensity map of the asymmetric deformation stretching band of the NH³⁺ group with nano-SEIRA spectrum.

The application of AFM-IR is a very good tool for a detailed description of the adsorption process and distribution of cysteine onto the corroded AuNPs-Ti surface.

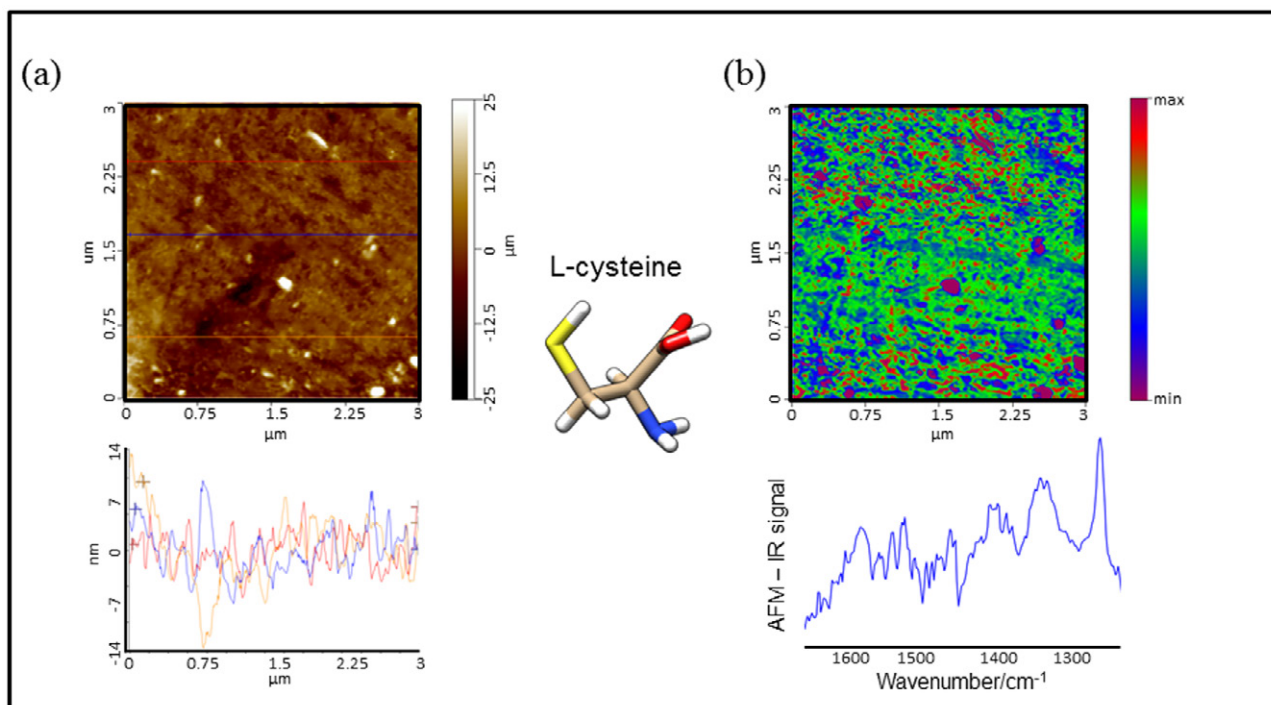


Figure 1. AFM topography $3 \mu\text{m} \times 3 \mu\text{m}$ of the corroded AuNPs-Ti surface with deposited Cys ($10^{-3}\text{M}/\text{PBS}/\text{pH}$ 5.0) with height profiles a) and AFM-IR intensity map of the band at 1586 cm^{-1} with nano-SEIRA spectrum of cysteine adsorbed on the corroded AuNPs-Ti surface (b).

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Funding Sources

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15 - Novel AFM-IR Analysis applied to cultural heritage samples

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This poster demonstrates the analytic capability of atomic force microscopy combined with infrared spectroscopy (AFM-IR) applied to art conservation science. Embedded pigments, painting cross-sections,

and reconstructed paint films have been studied. Pigment morphology and chemical variation are assessed and visualized, as are pigment-binder interactions and their variation under artificial ageing conditions. Of particular interest are the pigment-binder interactions and particle morphologies and distributions of azurite and smalt, due to their instability in some binders and demonstrated tendency to degrade. AFM-IR presents an optimal combination of sub-diffraction limit resolution of physical and chemical features of the sample surface that are difficult or impossible to analyze by conventional IR spectroscopy. As degradation often initially occurs on the surface of works, this surface-sensitive technique has important applications in understanding these processes. Furthermore, following removal of a small sample from a work, AFM-IR can be employed nondestructively, meaning that it is useful for further analysis on existing cross-section samples as well as reconstructions.

We present the results of an initial study of linseed oil oxidation and an additional analysis of azurite pigment in organic binding media. Linseed oil oxidation is shown to be structurally heterogeneous on the sub-micron scale, with rounded, regular domains present delineated by raised, web-like structures. These structures are significantly altered under ultraviolet-accelerated ageing. The results of analysis of azurite pigments demonstrate the particle size variation of different pigment grades and nanoscale mineral heterogeneity. This research demonstrates the utility of AFM-IR in studying the structure and ageing of historical samples.

16 - Miscibility and phase separation in PMMA/SAN blends investigated by nanoscale AFM-IR

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The miscibility and phase separation of poly(methyl methacrylate) (PMMA) and styreneacrylonitrile (SAN) have already been investigated using various methods. However, these methods have limitations that often result in inconsistent characterization. Consequently, the reasons for the dependence of miscibility on composition as well as on processing temperature have not yet been proved. The phase separation of PMMA/SAN blends was therefore investigated for the first time using a novel technique, nanoscale AFM-IR. Therefore, the phase morphology can be chemically identified and precisely classified within the nm-regime. The PMMA/SAN blends, on the other hand, were analyzed of their changes in morphology under different thermal treatments. It was possible to visualize and define the phase separation, as well as dependence of the miscibility on the mixing ratio. In the miscible domain, no two individual phases could be detected down to the nanometer range. It was shown that with increasing temperature, the morphology changes and two different phases are formed, where the phase boundaries can be sharply defined. The onset of these changes could be identified at temperatures of about 100 °C.

17 - Identifying reactivity variations on different facets in single Au nanocrystals.

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Metal nanoparticles play an essential role in heterogeneous catalysis. However, catalytically-active metal nanoparticles are heterogeneous in their nature and even within the simplest particles, structural differences exist and affect the overall performances of a catalyst. Fundamental understanding of the facet-dependent reactivity requires analysis at the single-particle level. This study identifies, using AFM-IR (Atomic Force Microscopy Infrared) mapping and 4-Nitrobenzenethiol (p-NTP) as probe molecule, the chemical reactivity on different facets in single Au nanocrystal. IR mapping revealed that p-NTP coverage is facet-dependent and higher coverage was identified on (110) facets, while lower coverage was detected on (111) facets (Figure.1).

Exposure of the sample to reducing conditions resulted in complete nitro-to-amine reduction on the (110) facets while on (111) facet both N-O and N-H vibrations were detected, implying that only partial reduction was achieved on these sites.

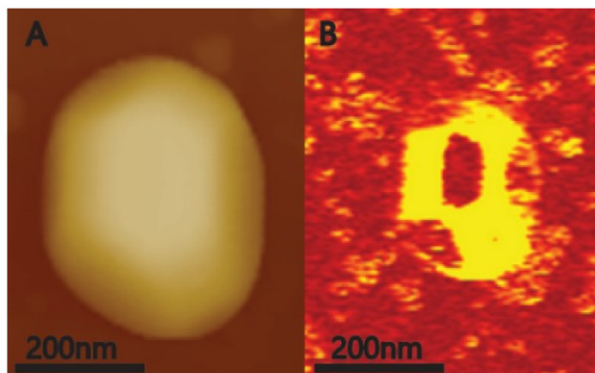


Figure 1. (a) AFM topography of Au nanocrystal coated with p-NTP, (b) IR mapping at 1336 cm^{-1} (correlated NO symmetric stretch), of the nanocrystal that is shown in a.

18 - Nanophotonic transducer for AFM-IR

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In an Atomic Force Microscopy based Infrared Spectroscopy (AFM-IR) system, the cantilever probe that can operate at high resonant frequency enables the measurement of chemical composition of the very thin sample down to molecular monolayer thickness, and allows to observe nanoscale dynamics in materials [1]. Such probe comes with the cost of difficulties to prepare the readout system when narrowing down the dimension of the cantilever to smaller than the deflection laser beam. This work proposes a novel AFM cantilever probe with embedded optical structure for force sensing. Different nanophotonic resonators based sensing structure are investigated. When the cantilever bends, the physical deformation and the stress induced refractive index change cause the resonance wavelength to shift. By detecting the shift, one can know the force between the tip and the sample, the cantilever deflection, thus the thermal expansion of the sample [2]. For the cantilever of 100 μm length, 6 μm width, 1.5 μm thickness with embedded uniform Waveguide Bragg Grating (WBG) of 320nm periodicity, 50nm corrugation depth, the simulation result shows 2 nm wavelength shift when 1 μN force is applied to the tip, and the shift scales linearly depending on the applied force. Besides the application in AFM-IR, this cantilever can also be optimized for use as the optical microphone in Photoacoustic Spectroscopy (PAS) for gas sensing.

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19 - Surface modification of titanium by Cu nanoparticles in the presence of amino acid

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The comprehensive electrochemical and spectroscopic investigations were performed, which allow for understanding and describing the processes that occur on a nano-modified Ti by Cu nanoparticles (CuNPs) in the presence and absence of tryptophan (Trp), exogenous amino acid [1]. In addition, copper (Cu) is a significant trace element in the human body, which plays many functions in physiological activities [2]. The deposition of a thin CuNPs layer on the Ti substrate improves the corrosion resistance of the substrate under simulated physiological conditions (phosphate-buffered saline (PBS) solution, pH = 7.4) at 37 °C). The addition of Trp to the corrosive environment drastically initiated the degradation of the CuNPs coating (formation of a Cu-Trp complex and nano-galvanic sites at the substrate/ CuNPs coating interface). The conformational changes of Trp on the corroded CuNPs-Ti surface have been studied by advanced surface-enhanced vibrational techniques. Trp interacted with the corroded CuNPs-Ti surface through the indole ring, which adopts a more/ less horizontal orientation and the protonated amine group in the presence of chloride and phosphate ions on the metallic surface. Figure 1 shows the topography of the Ti surface after sputtering of the CuNPs layer with the height profiles, and the topography of the corroded CuNPs-Ti surface with the presence of Trp together with the AFM-IR map. This map presents the intensity distribution of the characteristic band in the nano-SEIRA spectrum due to the vibrations of the terminal (NH³⁺)/(COO⁻) groups. The application of a combination of infrared spectroscopy with atomic force microscopy (AFM-IR) proved that Trp covered the bimetal surface and caused the significant degradation of the metallic surface.

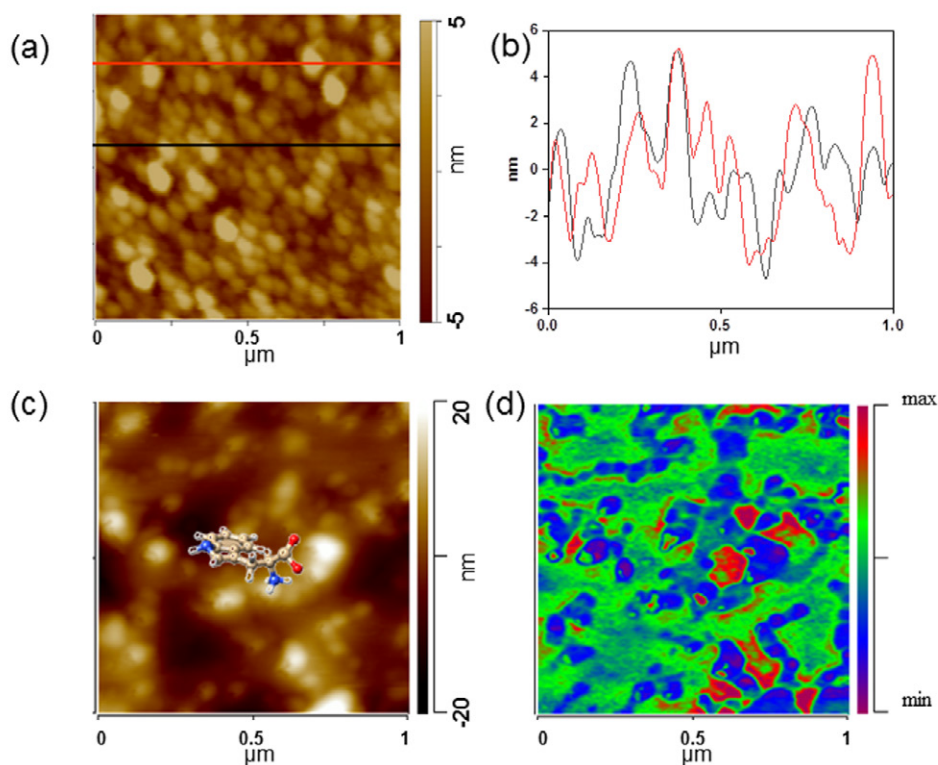


Figure 1. AFM topography (a) with height profiles of CuNPs-Ti surface (b) and AFM topography of the corroded CuNPs-Ti surface with deposited Trp (10^{-3} M/PBS/pH 7.4) (c) the AFM-IR intensity map of the band at 1655 cm^{-1} (d).

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