RamanFest

Paris | FRANCE

September
15-16
2022

International Conference on Advanced Applied Raman Spectroscopy

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INDEX

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FOREWORD

On behalf of the Organising and the International Scientific Committees, we take great pleasure in welcoming you to Paris (France) for this new edition of the RamanFest International Conference (RamanFest2022)

The 9th International Conference on Advanced Applied Raman Spectroscopy (RamanFest2022) will feature presentations from world-leading Raman experts and researchers using the technique across varied applications within life science, materials science, and energy and environmental analysis. It will bring together the world's Raman community to share, learn and discuss how Raman spectroscopy is being applied to today's problems and pioneering tomorrow's capabilities.

We are indebted to HORIBA Scientific for their help and financial support. We also would like to thank all the speakers, partners and participants that joined us in person this year.

Hope to see you again in the next edition of RamanFest.

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HORIBA

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In 2019 HORIBA has celebrated the 200th anniversary of its optical spectroscopy roots. The Maison Soleil was founded in 1819 by Jean-Baptiste Soleil, becoming in 1923 the company Jobin Yvon through association with Amédée Jobin and Gustave Yvon. The technical foundation given by the Maison Soleil and the subsequent Jobin Yvon company remains at the heart of HORIBA's spectroscopy products, which are renowned for their performance and quality.

SPEAKERS LIST

		PAGE
Ghulam Abbas (J. Heyrovský Institute of Physical Chemistry of CAS, Czech Republic) *In-situ Raman spectroelectrochemistry of graphene in concentrated aqueous electrolytes*	Poster	**61**
Mahebub Alam (Institute of Phsics of the Czech Academy of Sciences, Czech Republic) *Polarized Raman Spectroscopy of boron-doped diamond*	Poster	**62**
Martina Banchelli (IFAC-CNR, Italy) *SERS and molecular seed amplification to make diagnosis of Alzheimer's disease*	Oral	**34**
Charlotte Berrezueta (Fu Berlin, Germany) *Collective Vibrational Effects in Carbon Nanotube Coils*	Poster	**63**
Sylwia Berus (Institute of Physical Chemistry of the Polish Academy of Sciences, Poland) *SERS-based study supported by chemometric methods for the differential diagnosis of vaginal infections*	Oral	**35**
Carolin Borbeck (Heinrich-Heine-University, Germany) *A Fast Broadband Approach to the Analysis of Microplastics: Femtosecond Stimulated Raman Microscopy*	Oral	**36**
Anthony Boulanger (GreenTropism, France) *SERS & AI, an innovative combination for Virus Detection*	Invited	**19**
Maximilian Brinkmann (Refined Laser Systems GmbH, Germany) *High-speed Multicolor Stimulated Raman Imaging Enabled by a Compact and Robust Light Source*	Oral	**37**
Maximilian Brinkmann (Refined Laser Systems GmbH, Germany) *High-speed Multicolor Stimulated Raman Imaging Enabled by a Compact and Robust Light Source*	Poster	**64**
Cléophanie Brochard (C2N, France) *Heat transport in h-BN*	Poster	**65**
Thibault Brulé (HORIBA France SAS, France) *Raman microscopy : one solution for your application*	Oral	**38**
Thibault Brulé (HORIBA France SAS, France) *Defects in polymer multilayer films: A new way to investigate based on Raman microscopy*	Poster	**66**
Xueqin Chen (Lightcore Technologies, France) *Life Science in Live by Nonlinear Microscope and Endoscope*	Oral	**39**

		PAGE
Luka Pirker (J. Heyrovsky Institute of Physical Chemistry, Czech Republic) *Local Raman spectroscopic fingerprints of TMDC-metal interactions*	Oral	52
Jad Rabah (LISE Sorbonne Université, France) *Transient Electrochemical Tip Surface-Enhanced Raman Spectroscopy (EC-Tip-SERS): Concept and Applications in Electrocatalysis and Material Science*	Oral	53
Meryem Rahmani (IMMM, France) *Can a low-cost nano-rough gold substrate compete with commercial SERS substrates?*	Oral	54
Hervé Rigneault (Institut Fresnel, France) *Coherent Raman imaging for scientific and biomedical applications*	Keynote	17
Andrea Mario Rossi (INRiM, Italy) *Dielectrophoresis for Raman analysis in liquid: applications to bacteria and viruses*	Invited	30
Alessio Sacco (INRiM, Italy) *Interlaboratory comparison on relative quantification of titanium dioxide (TiO2) polymorphs in binary mixtures by Raman spectroscopy*	Oral	55
Pierre-Yves Sacré (University of Liège, Belgium) *Interest of Raman spectroscopy for the detection and analysis of poor-quality medicines*	Invited	31
Farnoush Salehtash (Institute of Physics, Slovak Academy of Sciences, Slovakia) *Surface Enhanced Raman Scattering study of MXene based glass substrates*	Poster	85
George Sarau (Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany) *Correlative Spectroscopy and Microscopy Analysis of Micro- and Nanoplastics and Their Effects on Cells and Tissues*	Oral	56
Iwan Schie (University of Applied Sciences - Jena, Germany) *Technical Innovations and Clinical Translation in Raman Spectroscopy*	Invited	32
Ambika Shorny (Technische Universität Wien, Austria) *Detection of nanoparticles by surface-enhanced Raman microscopy*	Poster	86
Dejan Skrelic (CNRS / Saint-Gobain Research Paris, France) *Python Toolkit for Visual Exploration of Raman Spectra*	Oral	57
Raphaël Strenaer (GREYC, France) *Thermal characterization of GaN-based HEMTs by using Raman spectroscopy and micro-Raman thermometers*	Oral	58
Amro Sweedan (Ben-Gurion University, Israel) *Gold Flakes based nanostructure as new SERS sensing platform*	Poster	87
Ivan T. Lucas (CNRS - Sorbonne Université, France) *Interfacial Instability in Operating Lithium-Ion Batteries Unraveled by SHINERS*	Invited	33

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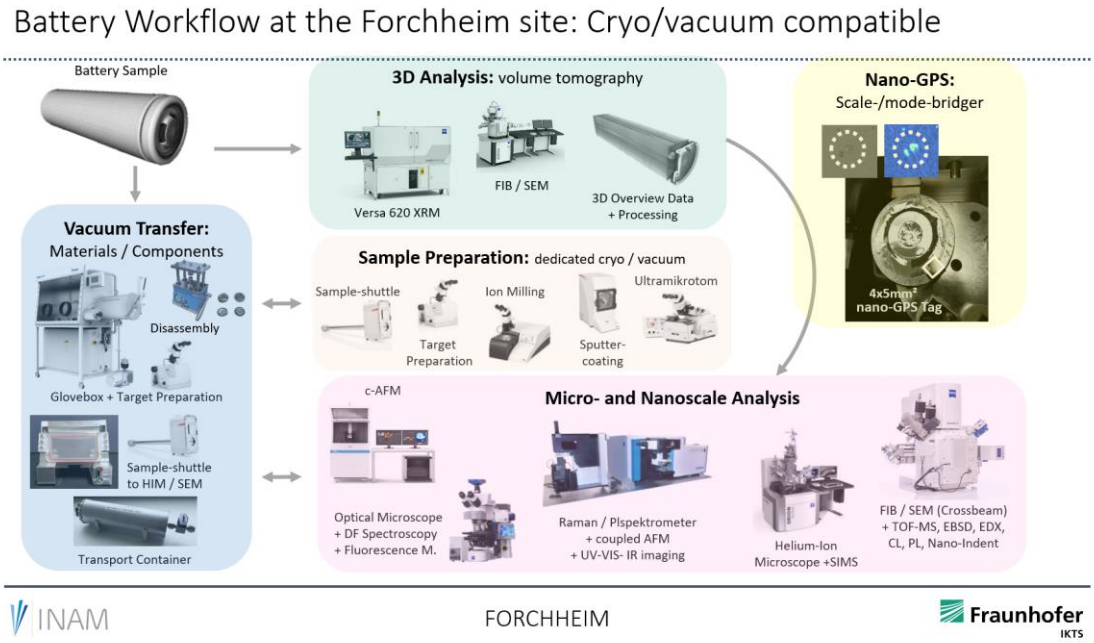
Multi-modal, scale bridging analytics in energy research

Energy systems like solarcells, fuel cells and batteries contain a variety of different atoms from all over the periodic system, thereby attributing to strongly varying materials and device properties. The materials are usually stacked in layers of varying thickness and are composed of micro- or nano-particles or consist in grains and phases embedded in complex matrix materials. All components contain a wealth of interfacial area which has tightly to be controlled for optimized performance. Our goal in energy research is to control material properties at all scales from macro to atomic scale and to optimize materials in a tight feedback loop with device manufacturers who optimize and control device performance. In this endeavor, control needs to be taken over composition, grain and particle sizes, interfacial properties, defect population, topological, electrical, mechanical, optical and compositional properties. In our lab in Forchheim, Nuremberg Metropolitan Area, Germany, which is built as a joint venture of the Fraunhofer Institute for Ceramics Materials and Systems – IKTS and the Institute for Nanotechnology and Correlative Microscopy – INAM and which profits from the labs@location status with Carl Zeiss Microscopy and the strategic demo-site collaboration with Leica Microsystems, Horiba Europe/Scientific, Park Systems and Photon Energy, we established a preparative workflow (Fig. 1) for energy materials which includes an inert transfer line from a glovebox over cutting, grinding, polishing and ion-milling steps all the way into microscopes and spectrometers as much as a cyro-workflow where needed, e.g. during ion-milling and electron microscopy. The analytics (Fig. 1) include imaging with electrons, ions, x-rays, light and probes in 2D and 3D (tomography) as well as spectroscopy (mass, Raman, infra-red) at length scales from macro to nano together with mechanical and topological testing as well as electrical, optical and compositional analysis. The underlying multi-modal, scale-bridging data will be analyzed correlatively and quantitatively with the help of the nanoGPS technology [1] and powerful database systems (KnowitallR) as well as workflow engines such as the XamFlowR platform powered by Lucid concept [2] and image recognition software powered by machine learning algorithms and statistical data evaluation tools. This analytics lab will be used to study even the most delicate energy materials comprehensively to give guidance to device optimization and to contribute with data to the creation of a digital twin.

References

[1] https://www.horiba.com/deu/scientific/products/detail/action/show/Product/nanogps-navyx-4959/
[2] https://www.lucid.ch/

Figures



Battery Workflow at the Forchheim site: Cryo/vacuum compatible

Battery Sample

Vacuum Transfer:
Materials / Components

Disassembly

Glovebox + Target Preparation

Sample-shuttle
to HIM / SEM

Transport Container

3D Analysis: volume tomography

Versa 620 XRM

FIB / SEM

3D Overview Data
+ Processing

Sample Preparation: dedicated cryo / vacuum

Sample-shuttle

Target
Preparation

Ion Milling

Sputter-
coating

Ultramikrotom

Micro- and Nanoscale Analysis

c-AFM

Optical Microscope
+ DF Spectroscopy
+ Fluorescence M.

Raman / Plspektrometer
+ coupled AFM
+ UV-VIS- IR imaging

Helium-Ion
Microscope +SIMS

FIB / SEM (Crossbeam)
+ TOF-MS, EBSD, EDX,
CL, PL, Nano-Indent

Nano-GPS:
Scale-/mode-bridger

4x5mm²
nano-GPS Tag

INAM

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Figure 1: Battery workflow from inert sample preparation and sample transfer, scale bridging, multi-modal micro- and nanoscale analysis and the nanoGPS technology [1] as an enabler for true data correlation at the nanoscale.

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Nanoscale materials characterization and metrology using Raman and PL

In semiconductor manufacturing, Raman spectroscopy is an attractive characterization technique for e.g. mechanical stress and composition, thanks to its versatility, high throughput and non-destructive character, but as an optical spectroscopic method it is inherently diffraction-limited. In order to re-enable the strengths of Raman spectroscopy at the nanometer scale, we exploit polarization-induced enhancement effects that focus the excitation light into the region of interest. As such, characterization of for instance mechanical stress and composition become possible on structures with dimensions far beyond the diffraction limit [1,2]. With the electric field confined to the small nanostructures under investigation, the penetration depth of the light is still much larger than the typical thickness of the layers in the stack, meaning that the totality of the structure is probed, and the intensity of the collected Raman scattering scales with that total volume. Therefore, when normalizing the signal from such structures to another reference signal in the spectrum (like Si-Si scattering from the substrate) we obtain a volumetric measurement of the amount of material present in the probed volume. This opens a completely new application domain for Raman spectroscopy as a dimensional measurement as we will demonstrate in a couple of examples (see Figure 1).

References

[1] T. Nuytten et al., APL Mat. 6 (2018) 058501
[2] J. Bogdanowicz et al., Appl. Phys. Lett. 108 (2016) 083106

Figures

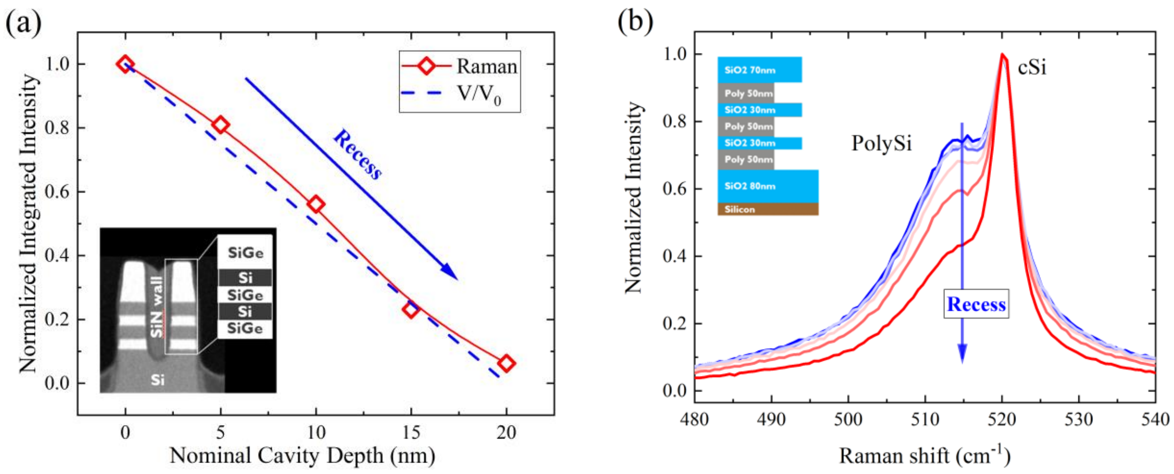

Figure 1: (a) Normalized integrated Si-Ge scattering intensity from a forksheet structure as a function of nominal cavity depth showing the strong sensitivity on etch depth. The inset shows a forksheet FET structure with the stacked Si and SiGe layers, where the SiGe is etched selectively from the sides. (b) Normalized Raman spectra for a stack of Si/polySi memory structures with a DOE of increasing etch rate from center to edge of the wafer sample, corresponding to the downward arrow in the plot.

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Coherent Raman imaging for scientific and biomedical applications.

Abstract:

We are developing coherent Raman microscopes and endoscopes suitable to perform chemical imaging for scientific and biomedical applications.

We have developed a picosecond laser source that can that can address simultaneously two vibrational wavenumbers for ratio-metric imaging and background rejection. The two wavenumbers can be addressed anywhere across the entire vibrational spectrum ($400cm^{-1}$ – $4000cm^{-1}$). The laser source is coupled to a ready to use beam scanning microscope enabling SRS, CARS and multiphoton microscopy. We are also developing a flexible endoscopes imaging probe featuring a diameter of 1.3mm at its distal end. The endoscope can perform CARS, SHG and multiphoton imaging for in vivo applications.

We will exemplify the ability of the developed microscope and endoscope technologies in various fields including cell imaging, drug penetration in skin, pharmaceutical imaging, food imaging... By targeting the CH_2 and CH_3 chemical bonds, we also demonstrate instantaneous stimulated Raman histology on freshly excised biopsies and on living organoids. Finally, we show the suitability of the systems to perform metabolic imaging on bacteria and drosophila fed with deuterated glucose.

SRS/CARS/multiphoton microscopes and endoscopes enable molecular detection and imaging with exquisite sensitivity (shot noise limited) and ratio-metric availability. By targeting simultaneously two vibrational frequencies that can be tuned anywhere across the vibrational spectrum. The microscopes and endoscopes are suitable to perform video rate chemical imaging for a broad range of scientific and medical applications.

References

[1] B. Sarri, R. Appay, S. Heuke, F. Poizat, F. Franchi, S. Boissonneau, F. Caillol, H. Dufour, D. Figarella-Branger, M. Giovaninni, and H. Rigneault, “Observation of the compatibility of stimulated Raman histology with pathology workflow and genome sequencing,” Translational Biophotonics n/a, e202000020 (2021). https://doi.org/10.1002/tbio.202000020

[2] B. Sarri, F. Poizat, S. Heuke, J. Wojak, F. Franchi, F. Caillol, M. Giovannini, and H. Rigneault, “Stimulated Raman histology: one to one comparison with standard hematoxylin and eosin staining,” Biomed. Opt. Express 10, 5378-5384 (2019). https://doi.org/10.1364/BOE.10.005378

[3] B. Sarri, R. Canonge, X. Audier, E. Simon, J. Wojak, F. Caillol, C. Cador, D. Marguet, F. Poizat, M. Giovannini, and H. Rigneault, “Fast stimulated Raman and second harmonic generation imaging for intraoperative gastro-intestinal cancer detection,” Scientific Reports 9, 10052 (2019). https://doi.org/10.1038/s41598-019-46489-x

[4] D. Septier, V. Mytskaniuk, R. Habert, D. Labat, K. Baudelle, A. Cassez, G. Brévalle-Wasilewski, M. Conforti, G. Bouwmans, H. Rigneault, and A. Kudlinski, “Label-free highly multimodal nonlinear endoscope,” Optics Express 30, 25020-25033 (2022). https://doi.org/10.1364/OE.462361

[5] A. Kudlinski, A. Cassez, O. Vanvincq, D. Septier, A. Pastre, R. Habert, K. Baudelle, M. Douay, V. Mytskaniuk, V. Tsvirkun, H. Rigneault, and G. Bouwmans, “Double clad tubular anti-resonant hollow core fiber for nonlinear microendoscopy,” Optics Express 28, 15062-15070 (2020). https://doi.org/10.1364/OE.389084

[6] A. Lombardini, V. Mytskaniuk, S. Sivankutty, E. R. Andresen, X. Chen, J. Wenger, M. Fabert, N. Joly, F. Louradour, A. Kudlinski, and H. Rigneault, “High-resolution multimodal flexible coherent Raman endoscope,” Light: Science & Applications 7, 10 (2018). https://doi.org/10.1038/s41377-018-0003-3 SMASH

Figure

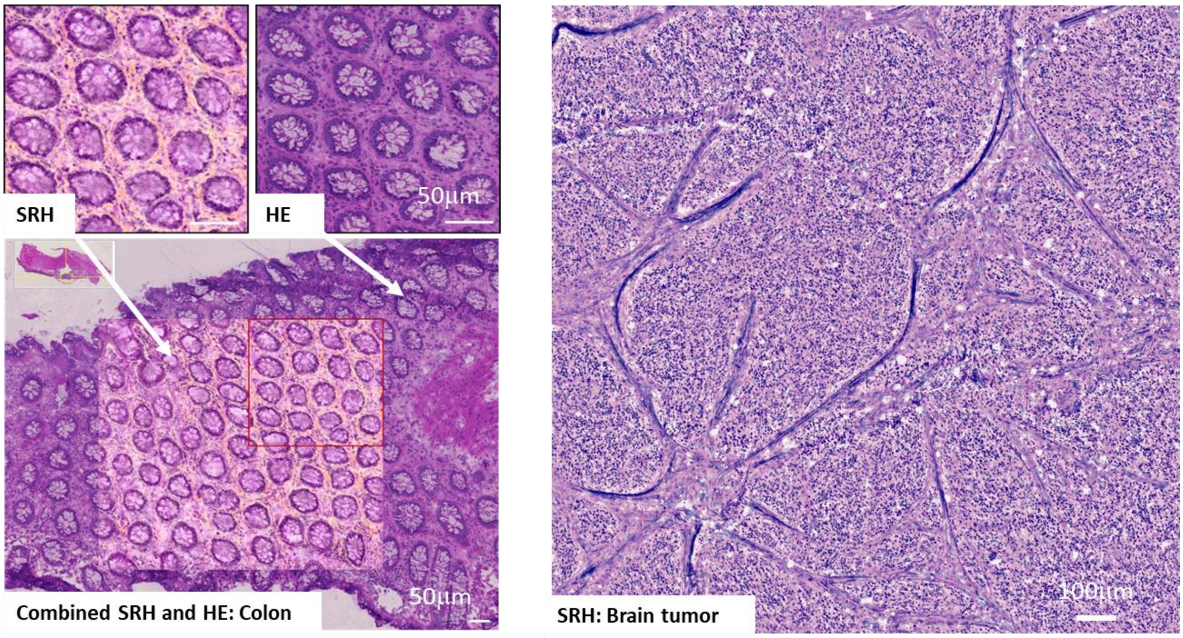

Figure 1: Right: Exemple of stimulated Raman histology (SRH) images as compared to standard hematoxylin and eosin images (HE). **Left:** SRH image of a brain tumor (1mm x 1mm, imaging time 2 minutes)

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SERS & AI, an innovative combination for Virus Detection

The world's history of SARS-CoV-2 pandemics has shown the need to adapt our pathogen detection technologies. Current detecting tools are indeed insufficient to face the flood of samples. As it requires a long time, many reagents and qualified personnel, RT-qPCR is not adapted when facing the need for rapid detection of a pathogen and laboratories often found themselves overloaded.

Surface Enhanced Raman Spectroscopy (SERS) has been described as a good detection tool for pathogens analysis, such as viruses or bacteria (1-3). This technique uses monochromatic light to excite a sample and get a spectral fingerprint signal in a matter of seconds.

Spectra obtained by SERS give a complete and complex fingerprint of the sample analyzed. Chemometrics and data science are here used to treat these signals to give a ultra-fast interpretation. We defined a protocol that combines SERS and AI to detect multiple viruses in order to bring an innovative and efficient technology for pathogen detection.

References

[1] T. J. Moore et al., Biosensors (Basel), vol. 8, no 2, mai 2018
[2] M. Chisanga et al.,, Applied Sciences, vol. 9, no 6, Art. no 6, janv. 2019
[3] C.-C. Andrei et al., Anal Bioanal Chem, vol. 413, no 5, p. 1417-1428, févr. 2021

Figures

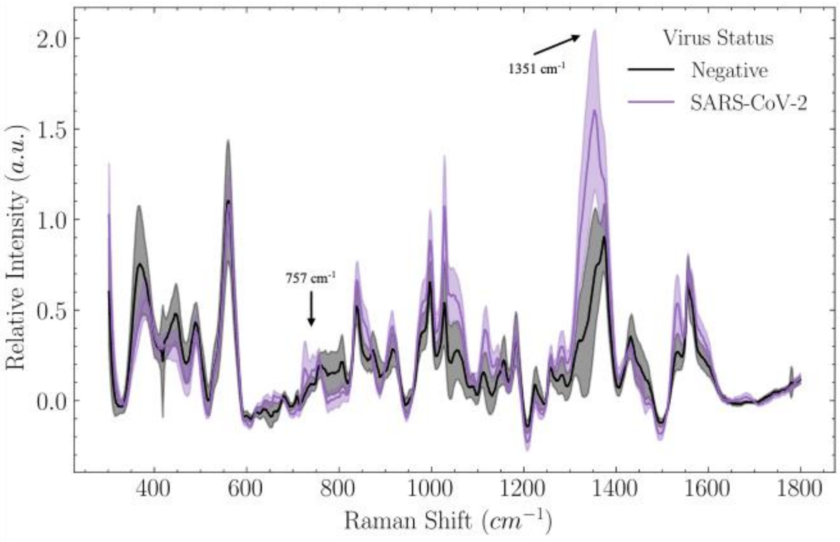

Figure 1: SERS mean spectra with standard deviation of coronavirus SARS-CoV-2 (purple) and negative (black) samples after preprocessing with SNV and ALS.

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Bioanalytical applications of Raman spectroscopy to follow active pharmaceutical and cosmetic ingredients

Development of novel pharmaceutical and cosmetic formulations is an important domain of biomedical research, both at academic and industrial scale. Including active pharmaceutical ingredients (API) or active cosmetic ingredients (ACI) within the forms composed of many components is intended to protect their activity from degradation upon storage and/or to improve their delivery to the site/organ of action. Consequently, it is important to follow the API or ACI qualitatively (at molecular state) and quantitatively (in terms of total quantity/concentration and relative spatial distribution) at different steps: (i) before, during and after formulation and (ii) after administration, in cells, tissues and/or fluids.

Among analytical techniques appropriate for these tasks, few are as versatile and flexible as Raman spectroscopy which is known to enable a non- invasive analysis *in situ*, with both high molecular/structural specificity and satisfactory accuracy for quantification. In addition, macroscopic, microscopic and remote probing through optical fibers Raman measurement modalities are available and thus are applicable in various contexts, from R&D to process analytical technology (PAT). The present talk will illustrate the use of Raman-based bioanalytical approaches in the domains of pharmaceutical [1,2], bio-pharmaceutical [3,4] and cosmetic [5,6] domains, starting from quality control before and after formulation and going to the API/ACI release and delivery to cells and tissues.

References

[1] Del Genio V, Falanga A, Allard-Vannier E, Hervé-Aubert K, Leone M, Bellavita R, Uzbekov R, Chourpa I, Galdiero S, Pharmaceutics, 14(8) (2022) 1544.
[2] Makki AA, Elderderi S, Massot V, Respaud R, Byrne HJ, Tauber C, Bertrand D, Mohammed E, Chourpa I, Bonnier F, Talanta, 228 (2021) 122137.
[3] Makki AA, Massot V, Byrne HJ, Respaud R, Bertrand D, Mohammed E, Chourpa I, Bonnier F, J Pharm Biomed Anal. 194 (2021) 113734.
[4] Rayyad A, Makki AA, Chourpa I, Massot V, Bonnier F, Talanta, 250 (2022) 123692.
[5] Kichou H, Munnier E, Dancik Y, Kemel K, Byrne HJ, Tfayli A, Bertrand D, Soucé M, Chourpa I, Bonnier F, Molecules 27(9) (2022), 2843.
[6] Van Gheluwe L, Munnier E, Kichou H, Kemel K, Mahut F, Vayer M, Sinturel C, Byrne HJ, Yvergnaux F, Chourpa I, Bonnier F, Molecules, 26(24) (2021), 7440.

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20 years of on-site Raman analysis of works of art: successes, difficulties and prospects

The study, in particular of the state of conservation, and the authentication of works of art are issues in full development and Raman microspectroscopy in conjunction with X-ray fluorescence are the reference techniques due to their perfectly non-invasive character, and the availability of mobile instruments. Although mobile instruments have been available for more than 20 years, their use has only recently exploded with the tightening of formalities allowing the movement of valuable objects and changes in practices. Our team having been the first to developp the Raman analysis of works of art, whether in the laboratory with the development of the MOLE in 1975 at LASIR [1,2] and on site from the 2000s [3, 4], we will focus the presentation on fire arts objects, most of which are enameled (metal, glass or ceramic). These sophisticated objects were technological achievements at their time of production, made for the elite, traded very early on at long distance, and their value which can reach several millions of € imposes on-site and non-invasive procedures. Their Raman analysis requires the use of high-performance instruments such as the HE532 and the Axial due to the simultaneous presence of vitreous phases generating a signature of broad bands and crystalline phases giving narrow peaks but mainly at low wavenumbers. With the development of particular procedures (use of sophisticated optics, micrometric stages, subtraction of the continuous background, analysis of proton corrosion, multivariate analysis) and an understanding/modeling of the spectra, the parameters of processing (temperature) are deduced [5 -8] and restorations/fakes/copies are identified.

References

[1] Delhaye M., Dhamelincourt P. J. Raman Spectrosc. 3 (1975) 33-43.
[2] Colomban P. L'Industrie Céramique 734 (1979) 815-820.
[3] Colomban P., Milande V., Le Bihan L. J. Raman Spectrosc. 35(7) (2004) 527-535.
[4] Colomban P., Tournié A. J. Cult. Her. 8(3) (2007) 242-256.
[5] Colomban P. J. Raman Spectrosc., 43(6) (2012) 1529–1535.
[6] Colomban, P. J. Non-Crystalline Solids 323(1-3) (2003) 180-187.
[7] Labet V., Colomban P. J. Non-Crystalline Solids 370 (2013) 10-17.
[8] Colomban P., Kirmizi . B, Zhao, B., Clais J.- B., Yang Y., Droguet V. Coatings, 10 (2020) 471.

Figures

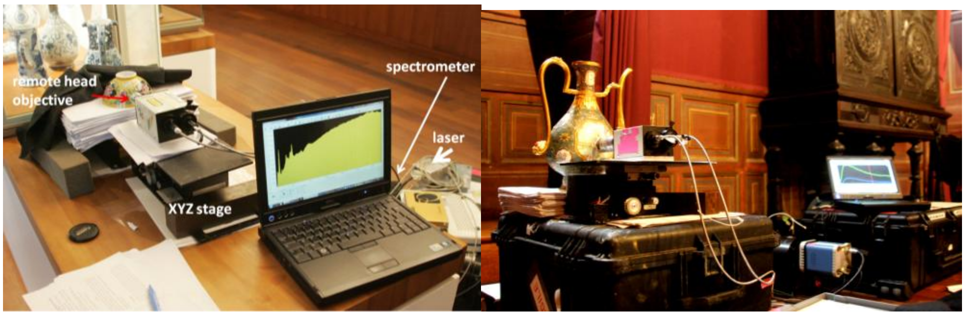

Figure 1: On-site Raman analysis using HE532 mobile set-up.

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Raman spectroscopy and imaging of “natural” gas hydrates

The natural occurrence of large quantities of gas hydrates in deep oceans, permafrost and plausibly in planets or comets of the solar system, is certainly at the origin of numerous developments and researches on gas hydrates in fields ranging from physical-chemistry, geosciences or astrophysics to chemical engineering and innovative technologies [1,2]. Gas hydrates are ice-like systems made of water molecules forming nano-cages stabilized by the encapsulation of foreign molecules. At a fundamental level, the understanding of their physical-chemistry properties (trapped-gas selectivity, kinetics formation mechanism, influence of sedimentary matrices, etc.) is of prime importance to track the evolution of the abundances of species taking part in the compositions of hydrate-bearing deposits not only on Earth, but also potentially on extraterrestrial bodies. The understanding of their molecular interactions plays a key role, requiring multi-scale approaches and the combination of advanced experimental and theoretical approaches for which Raman spectroscopy and imaging plays a key role. After a short review of some of the recent physico-chemical achievements (e.g. metastability [3,4,5], molecular selectivity [6,7], formation kinetics [8,9], etc.) relevant in gas hydrates sciences, the presentation will focus on the contribution of Raman spectroscopy and imaging for investigating gas hydrates naturally occurring in deep-ocean sea-floors [9,10].

References

[1] Broseta et al, Gas hydrates 1, Wiley-ISTE: London (2017)
[2] Ruffine et al, Gas hydrates 2, Wiley-ISTE: London (2018)
[3] Métais et al, J. Phys. Chem. C 125(11) 6433-6441 (2021)
[4] Petuya et al, J. Chem. Phys. 150(18) 184705 (2019)
[5] Petuya et al, J. Phys. Chem. C 122(1) 566 –573 (2018)
[6] Petuya et al, J. Phys. Chem. C 123(8) 4871-4878 (2019)
[7] Petuya et al, Chem. Comm. 54 4290-4293 (2018)
[8] Métais et al, to be submitted (2022).
[9] Guimpier et al, to be submitted (2022).
[10] Agnissan et al, to be submitted (2022).

Figures

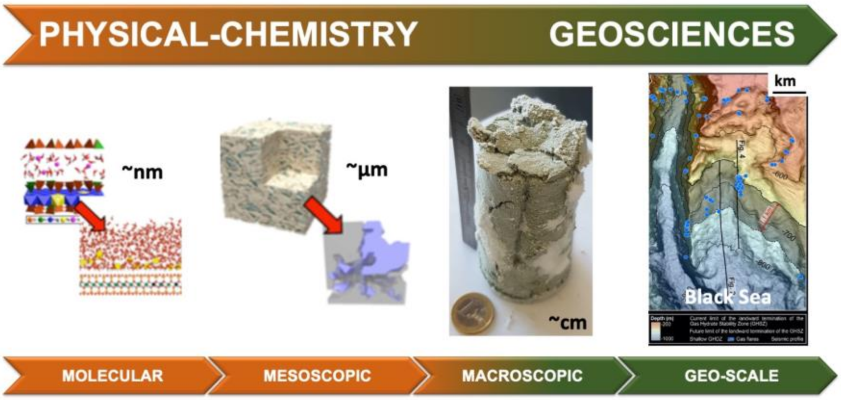

Figure 1: *Illustration of the multi-scale investigations required for understanding the formation of gas hydrate in natural environment.*

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Directional beaming and localization effects in Raman light generated in random array of silicon nanowires

Disordered photonics is a new research field that is attracting a large interest worldwide for its direct implications in concrete applications such as, diagnostics [1], photovoltaics [2] and new light sources [3]. This is because the very multiple scattering nature and the light transport properties of random media allow optical performances often superior to those offered by ordered photonic structures [4]. On the other hand, the diffusive propagation of light through disordered materials gives rise to fascinating and sometimes unexpected interference phenomena surviving also in the inelastic scattering regime [5]. Here we will present recent experimental results where disordered arrays of silicon nanowires are used to generate and beam directional coherent Raman light [6]. We show the direct visualization of the weakly localized Raman radiation by both real- and momentum-space microscopy, that permitted us to gain insight on the mechanisms ruling the light transport through the random media. These results pave the way for the development of next generation of new light sources based on both the coherent control of directional beaming and the fine frequency tuning.

References

[1] J. Bertolotti, E.G. van Putten, C. Blum, A. Lagendijk, W.L. Vos, and A.P. Mosk. *Non-invasive imaging through opaque scattering layers*. Nature 491: 232-234, 2012.

[2] O. L. Muskens, J. G. Rivas, R. E. Algra, E. P. A. M. Bakkers, and A. Lagendijk, *Design of Light Scattering in Nanowire Materials for Photovoltaic Applications*, Nano Lett. 8: 2638–2642, 2008.

[3] D. S. Wiersma. *The physics and applications of random lasers*, Nat. Phys. 4: 359–367, 2008.

[4] B. Fazio, P. Artoni, M.A. Iatì, C. D'Andrea, M.J. Lo Faro, S. Del Sorbo, S. Pirotta, P.G. Gucciardi, P. Musumeci, C.S. Vasi, R. Saija, M. Galli, F. Priolo, and A. Irrera. *Strongly Enhanced Light Trapping in a Two-dimensional Silicon Nanowire Random Fractal Array*. Light: Science & Applications,5: e16062, 2016.

[5] B. Fazio, A. Irrera, S. Pirotta, C. D’Andrea, S. Del Sorbo, M.J. Lo Faro, P.G. Gucciardi, M.A. Iatì, R. Saija, M.Patrini, P. Musumeci, C.S. Vasi, D.S. Wiersma, M. Galli, and F. Priolo. *Coherent Backscattering of Raman Light.* Nature Photonics 11: 170-176, 2017.

[6] M.J. Lo Faro, G. Ruello, A.A. Leonardi, D. Morganti, A. Irrera, F. Priolo, S. Gigan, G. Volpe, and B. Fazio. *Visualization of directional beaming of weakly localized Raman from a random network of silicon nanowires*. Advanced Science, 2100139, 1-11, 2021. DOI 10.1002/advs.202100139.

Figures

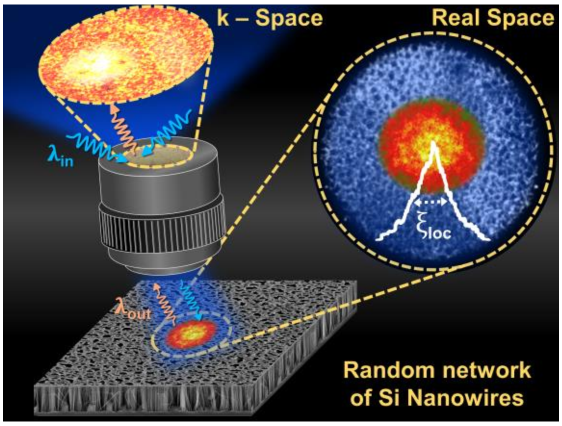

Figure 1: Visualization of coherent Raman light arising from a Si NWs random network: localized light paths in the real space and directional beaming in the momentum space.

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Designing aggregates of metallic nano-particles to generate tunable Resonant Raman structures

Abstract

Our group develops a new approach combining an Atomic Force Microscope and a confocal-Raman microscope where AFM microscope is used to image and to manipulate nano-particles under the confocal optical microscope coupled at the Raman spectrometer [1-2]. Our optical device allows us to scan the resonance effects by tuning the wavelengths of excitation.

At first, this talk will begin with the results obtained with some home designed symmetric structures of assembling of gold nano-particles (AuNPs) [1], in the vicinity of a single and isolated carbon nanotube (CNT). The super-resolved Raman spectra will be discussed as a function of the different sub-wavelength-scale geometries of AuNPs aggregates. The different interactions between AuNPs aggregates and the CNTs, including their impact on resonance effects will investigated. In particular, we will focus on the enhancement of the local electrical field by metallic nano-structures to probe single objects.

Secondly, at larger scale, this talk will finish with network of linear assemblies of metallic NPs. In line with the approach known as shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) [3], in which Raman signal amplification of analytes is provided by metallic NPs with an ultrathin dielectric shell, this presentation will report on a Surface-Enhanced Raman Spectroscopy (SERS) substrate consisting of periodic lines of metallic NPs embedded in dielectric surfaces for enhancing Raman signals [4]. These PLANEDSERS (fig. 1.) substrates produced by glancing-angle ion-beam sputtering deposition on nano-rippled patterns present polarization-dependent near field amplifying regions thanks to localized plasmon resonances of the NPs assembly. This design of a substrate-platform without chemical specificity to enhance in equal manner all the weak Raman signals of usual organic molecules.

Finally, we will conclude with another nano-thin 3D gold assembly [5], lamellar nanogold thin films, allowing the monitoring of traces in the vapor phase with enhancements aided by "remote Raman" scattering processes [6].

References

[1] A. D’Orlando, M. Bayle , G. Louarn and B. Humbert* Materials, Materials (2019) 12(9), 1372"AFM-Nano Manipulation of Plasmonic Molecules Used as “Nano-Lens” to Enhance Raman of Individual Nano-Objects Materials" (2019) 12(9), 1372; (doi.org/10.3390/ma12091372)

[2] A. D'Orlando*, J.Y. Mevellec, G. Louarn and B. Humbert* J. Phys. Chem. C (2020) 124, 4, 2705-2711 “AFM Nano-Manipulation by Confocal Raman Multiwavelength Spectroscopy: Application at the Monitoring of Resonance Profile Excitation Changes of Manipulated Carbon Nanotube”, (doi.org/10.1021/acs.jpcc.9b10096).

[3] Florian Forato, Somayeh Talebzadeh, Nicolas Rousseau, Jean-Yves Mevellec, Bruno Bujoli, D. Andrew Knight, Clémence Queffélec* and Bernard Humbert*, PCCP 21 (2019) 3066 "Functionalized core–shell Ag@TiO2 nanoparticles for enhanced Raman spectroscopy: a sensitive detection method for Cu(II) ions" (doi: 10.1039/c8cp07504b

[4] Sophie Camelio, David Babonneau, Elliot Vandenhecke Guy Louarn, and Bernard Humbert*, Nanoscale Advances, (2021), “Linear chains of Ag nanoparticles embedded in dielectric films for SERS applications in analytical chemistry” DOI: 10.1039/d1na00586c

[5] Adrien Chauvin, Marta Lafuente, Jean Yves Mevellec, Reyes Mallada, Bernard Humbert*, Maria Pilar Pina, Pierre-Yves Tessier* and Abdelaziz El Mel, Nanoscale, (2020), 12, 12602 “Lamellar nanoporous gold thin films with tunable porosity for ultrasensitive SERS detection in liquid and gas phase” DOI: 10.1039/d0nr01721c

[6] Issraa Shahine , Jean-Yves Mevellec , Mireille Richard-Plouet , Bernard Humbert* and Pierre-Yves Tessier* Submitted Nanoscale (2022).

Figures

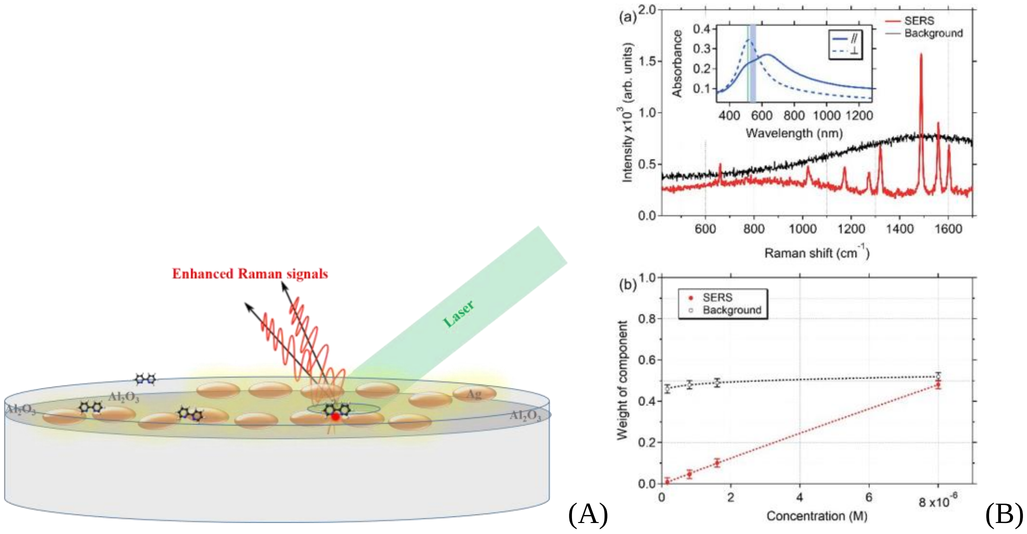

Figure 1: ‘PLANEDSERS’ substrates (schemed in A) as washable and reusable chemical sensors with a good level of repeatability (B)

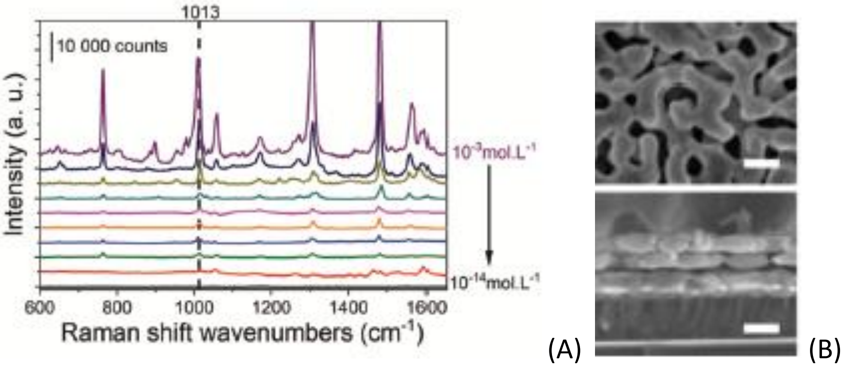

Figure 2: SERS Spectra recorded between 10-4 M and 10-14 M of bipyridine with nano-thin film of porous gold substrate (SEM images at right, top=plan view and down= cross section, scale bar=100 nm) .

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Visualizing Surface Phase Separation in PS-PMMA Polymer Blends at the Nanoscale using Tip-enhanced Raman Spectroscopy

Phase-separated polymer blend films are an important class of functional materials with numerous technological applications including solar cells [1], coatings [2], and biotechnology [3]. These technologies are underpinned by precise control of phase separation at the nanometer length-scales, which is highly challenging to visualize using conventional analytical tools. In this work, we show that tip-enhanced Raman spectroscopy (TERS), in combination with AFM, confocal Raman spectroscopy, and XPS, is a sensitive nanoanalytical method to determine lateral and vertical phase-separation in polystyrene (PS)-poly(methyl methacrylate) (PMMA) polymer blend films (Figure 1a) [4]. Correlative topographical, molecular, and elemental information obtained using the combination of techniques is able to reveal a vertical phase separation of the polymers within the top *ca.* 20 nm of the blend surface in addition to the lateral phase separation in the bulk. Furthermore, complementary TERS and XPS measurements reveal the presence of PMMA within 9.2 nm of the surface and PS at the sub-surface of the polymer blend as schematically illustrated in Figure 1b. These results show that correlative topographical, molecular, and elemental information can provide a complete picture of the lateral and vertical phase separation in polymer-blends, which cannot be determined by any single technique alone. This work demonstrates the potential of TERS to be a powerful complementary analytical tool for nanoscale polymer characterization.

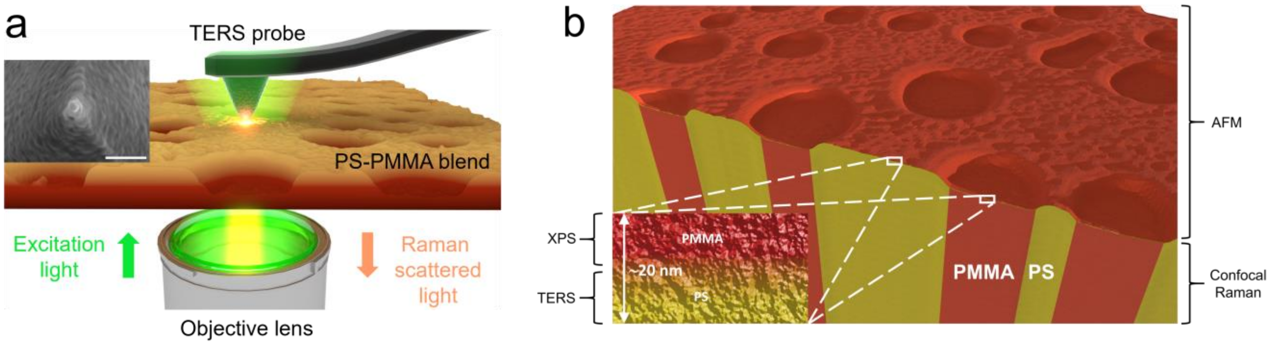

Figure 1: (a) Scheme of the transmission-mode AFM-TERS setup used for AFM, confocal Raman and TERS measurements in this study. Inset displays a SEM image of a representative Ag-coated TERS probe. Inset scale bar: 300 nm. (b) Schematic illustration of the proposed PS-PMMA blend structure based on the correlative AFM, confocal Raman, TERS and XPS measurements. Laterally phase-separated PS and PMMA domains revealed by AFM and confocal Raman imaging are covered with a continuous surface layer of vertically phase-separated PMMA and PS revealed by XPS and TERS, as shown in the inset.

References

[1] Moons, E., J. Phys. Condens. Matter 2002, 14 (47), 12235–12260
[2] Li, X.; Gao, J.; Xue, L.; Han, Y., Adv. Funct. Mater. 2010, 20 (2), 259–265.
[3] Budkowski, A. et al., J. Appl. Polym. Sci. 2012, 125 (6), 4275–4284
[4] Mrđenović, D.; Abbott, D.; Mougel, V.; Su, W.; Kumar, N.; Zenobi, R., ACS Appl. Mater. Interfaces 2022, 14, 21, 24938–24945

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Determination of free carrier concentration of polar semiconductors using LOPC modes: an example of InP

Free carrier concentration is one of the important properties of semiconductor devices/materials that may directly affect the performance of several applications in microelectronic and optoelectronic fields such as photodetector, lasers and light-emitting diodes [1]. This property therefore needs to be precisely controlled and measured. Conventional techniques (Hall Effect measurements and C-V characterization) can provide accurate results but usually require a time-consuming and/or destructive sample preparation. In polar semiconductors such as GaN, GaAs, InP, SiC, etc., the coupling between the longitudinal-optical phonon mode (LO) and the collective oscillations of the free carrier systems (plasmons) results in the so-called LO phonon-plasmon coupled modes (LOPC) [2-4]. This spectral feature, which strongly depends on the free carrier concentration, makes Raman spectroscopy an alternative nondestructive and contactless technique for rapid determination of doping concentration and can be used upon process validation and/ormass production. It is to note that, depending on the nature of the material as well as the doping type (n- or p-type), the evolution of LOPC modes vary differently as varying free carrier concentration. The LOPC consist of two branches: L^- and L^+ at low and high frequency, respectively. In general, the free carrier concentration can be deduced from L^+ peak position by fitting Raman spectral data to theoretical mathematic equations [2-4]. However, the doping concentration measured by different theoretical models existing in literature (and associated adjustable parameters) may present a significant variation (up to > 30%) [2]. Thus, establishing a calibration curve dedicated for an interesting concentration range is still needed to ensure the highest accuracy of quantitative measurement. The simplest way is correlating directly the spectral parameters measured at a given experimental configuration to the carrier concentrations obtained from a conventional method. Among the aforementioned semiconductors, the LOPC modes of InP is sensitive the most to the measurement conditions, especially the excitation wavelength and power due to the photogenerated carrier phenomenon [4]. Knowing the impact of different measurement parameters is primordial for accurate quantitative measurements. In this presentation, we present Raman analyses of n-doped bulk InP samples of various carrier concentrations performed with different configurations to illustrate their impact. The free carrier concentration deduced by Raman analyses is then compared to results of Hall Effect measurements. Finally, we present the calibration data linking directly the L^+ peak position to the carrier concentration obtained from Hall Effect measurements.

References

[1] Ghyselen, Bruno, et al., physica status solidi (a) 219.4 (2022): 2100543.
[2] Ochoa et al., Journal of applied physics 128.7 (2020): 075703.
[3] Haboeck, U., et al., Physica status solidi (c) 6 (2003): 1710-1731.
[4] Artús, L., et al., Physical Review B 60.8 (1999): 5456.

Figures

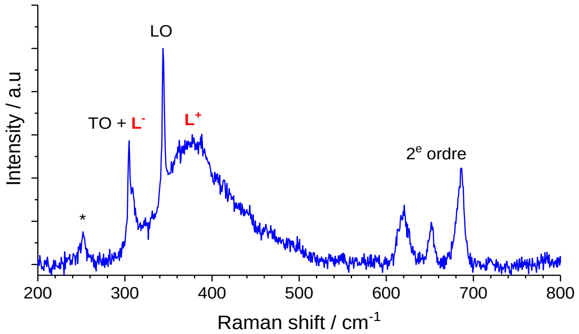

Figure 1: Raman spectrum of n-doped InP showing phonon and LOPC modes (L^- and L^+).

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Raman spectroscopy and TERS applied to energy storage and conversion materials

The quest for facile, non-destructive chemical analysis techniques that can provide microscopic insights into the phase evolution of materials has been the driving force for many successes in the research community within the last decades. Despite this progress, some of the most powerful techniques, such as current isotopic ion exchange methods, in situ TEM, and a collection of synchrotron radiation-based techniques, are quite complex, limiting easy access to crucial data for creating high-performance devices for energy harvesting and storage. Raman spectroscopy is a widely used optical technique able to provide quantitative chemical and structural information about the material under investigation in a fast, non-destructive manner.

In this work, we show two different applications of Raman spectroscopy to the evaluation of materials in the field of energy. In a first case of study, we present our recent advances in the utilization of Tip-Enhanced Raman Spectroscopy (TERS) for the study of the distribution of species in the surface of Li-ion battery cathodes. We show the high potential of TERS for studying phase evolution at grain boundaries thanks to the combination of the chemical sensitivity of Raman spectroscopy with high spatial resolution of scanning probe microscopy (SPM). In a second application, we show a novel implementation of Raman spectroscopy for the study of the oxygen diffusion in mixed-ionic-electronic (MIEC) electrodes for Solid Oxide Cells (SOCs). In this case, the sensitivity of the technique to the atomic mass of the involved species is exploited for studying the oxygen incorporation on thin films using O18 isotope as tracer.

Acknowledgements

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Hot photoluminescence and Raman processes in symmetric and asymmetric monolayer semiconductors

Energy relaxation of photo-excited charge carriers is of significant fundamental interest and crucial for the performance of layered semiconductors in optoelectronics. I will show how ultra-low frequency Raman spectroscopy can be used for the investigation of the primary stages of carrier relaxation in a layered semiconductor. A series of periodic maxima in the hot photoluminescence intensity with a period of ~15 meV, stemming from energy states higher than the exciton state is revealed for both below (Stokes) and above (anti-Stokes) the laser excitation energy (Figure1a,b).[1] These are assigned to phonon cascades, whereby carriers undergo phonon-induced transitions between real states above the free-carrier gap with a probability of radiative recombination at each step and provide information on the relaxation pathway in the Brillouin zone.
Phonon cascades are also observed in novel, high-quality Janus SeMoS monolayers with a broken out-of-plane mirror symmetry and an in-built electric dipole. I will also discuss how the structure of these asymmetric monolayers can be assessed by Raman spectroscopy, showing a striking difference in the vibrational properties between Janus SeMoS and random MoSSe alloys (Figure1c). [2,3]

References

[1] I. Paradisanos, G. Wang et al., Nat Commun, 12 (2021) 538
[2] M. M. Petric, M Kremser M. Barbone et al., Phys Rev B, 103 (2021) 035414
[3] Z. Gan, I. Paradisanos et al., arXiv:2205.04751 (2022)

Figures

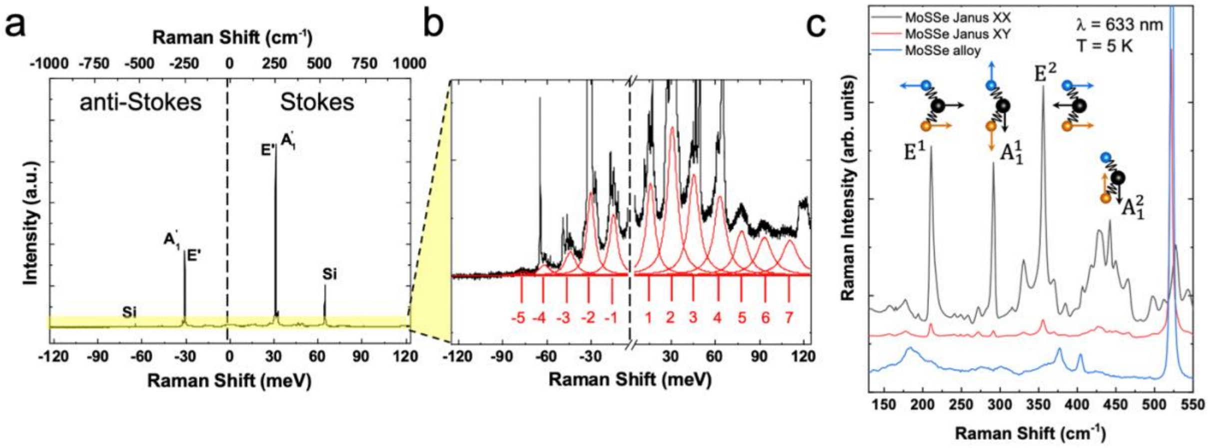

Figure 1: a) Emission and scattering spectrum of 1L-WSe$_2$ as a function of energy shift with respect to the excitation laser (here set to zero). **b)** Magnified portion of the spectrum in yellow in **a**. This reveals 7 periodic Stokes peaks and 5 anti-Stokes, assigned to phonon cascades. c) Comparison of Raman scattering data between SeMoS Janus monolayer (black and red graphs correspond to co- and cross- polarized detection) and MoSSe alloy monolayer (blue graph) which shows MoS$_2$-like doublet around 400 cm^{-1}. The main identified modes for the Janus sample are marked.

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Dielectrophoresis for Raman analysis in liquid: applications to bacteria and viruses

Raman microspectroscopy has recently been employed for the characterization of an increasing number of biological and environmental specimens. The speed and non-destructivity of the technique and its compatibility with water matrices can be exploited for live measurements on time-sensitive reactions, degradation, structural changes, drug uptake, vitality, and more. Dielectrophoresis (DEP) is the motion of dielectric particles by non-uniform electric fields [1]. DEP was employed to manipulate biological suspensions to locally concentrate the analytes to maximize Raman signal using a specially built cell. The design of this device was optimized by measuring polymer beads of various sub-micrometer sizes; Raman-DEP was then applied to live bacteria and active viruses in biologically compatible mediums.
The characterization of different bacterial strains, namely *E. coli*, *S. aureus* and *P. aeruginosa*, was carried out; DEP-aided Raman was then applied on *E. coli* treated with the commonly prescribed antibiotic ciprofloxacin (1 µg/ml, the minimum inhibitory concentration in the conditions of the experiment) proved that spectral changes in the bacterial chemical fingerprint due to the mode of action of the antibiotic were detectable after only one hour of treatment (traditional methods require 24 hours or more). Furthermore, with multivariate spectral analysis it was possible to create a test to determine antibiotic resistance and biocide-induced cross-tolerance of bacteria, that was validated by standard microbiological assays methods [2].
Moreover, DEP allowed the acquisition of conventional Raman spectra on different purified active viruses in liquid, and without the use of plasmonic enhancing surfaces or particles; a Raman spectral library of viruses was achieved. This method could allow the live study of the responses of isolated and inoculated viruses to conditions and chemicals, paving the way to the employment of Raman to new frontiers.

References

[1] Schröder, U.C., Ramoji, A., Glaser, U., Sachse, S., Leiterer, C., Csaki, A., Hübner, U., Fritzsche, W., Pfister, W., Bauer, M. and Popp, J., *Analytical Chemistry*, **85**, 22 (2013), 10717-10724.
[2] Barzan, G., Sacco, A., Mandrile, L., Giovannozzi, A.M., Brown, J., Portesi, C., Alexander, M.R., Williams, P., Hardie, K.R. and Rossi, A.M., *Sensors and Actuators B: Chemical*, **309** (2020), 127774.

Figures

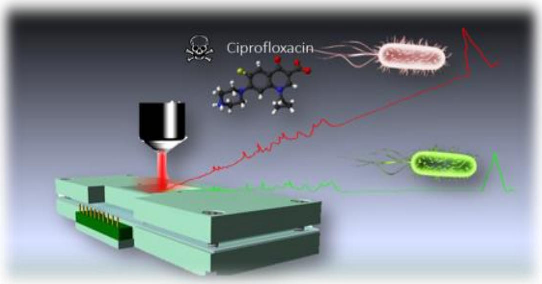

Figure 1: DEP device applied to Raman analysis a bacterial suspension.

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Interest of Raman spectroscopy for the detection and analysis of poor-quality medicines

Access to quality medicines is an essential right of the patients. However, in 2017, the World Health Organization estimated that 1 in 10 medical products circulating in low- and middle-income countries is either substandard or falsified. This reinforces the fact that post-marketing surveillance (PMS) of medical products by strong national regulatory authorities (NRA) is crucial. To achieve an efficient PMS, the NRA need analytical tools at the inspection, screening, confirmatory and forensics levels to control the physicochemical properties of the samples.

Among the analytical tools available, Raman spectroscopy is particularly interesting because of its spectral specificity and the wide variety of acquisition modes available. Handheld devices may be used directly on the field to confirm the presence of a specific active pharmaceutical ingredient (API) in a formulation [1]. Thanks to databases of pure ingredients, it is also possible to identify the compound present when a wrong API is present [2]. Recent developments have extended the applicability of handheld devices to the analysis of fluorescent chemicals and the analysis through barriers [3]. The detection of substandard medicines is also made possible with the construction of regression chemometrics models [4].

Benchtop systems and among them imaging systems are particularly useful in the confirmatory and forensic steps. Indeed, the imaging systems enable the visualization and identification of a large range of both organic and inorganic compounds used as API or excipients [5]. In addition, thanks to the high spatial resolution, it allows the detection of trace contaminants. This information may be of particular interest during prosecutions and the clustering of criminal cases. Nevertheless, the extraction of the relevant information from the raw measurements requires once again intensive work by highly trained staff.

In conclusion, Raman spectroscopy have particularly interesting features for the PMS of medicines.

References

[1] Deidda R., Sacré P.-Y., Clavaud M., Coïc L., Avohou H., Hubert Ph., Ziemons E., TrAC Trends in Analytical Chemistry, 114 (2019) 251-259
[2] Ciza P., Sacré P.-Y., Waffo C., Coïc L., Avohou H., Mbinze J., Ngono R., Marini R., Hubert Ph., Ziemons E., Talanta, 202 (2019) 469-478
[3] Alaoui Mansouri M., Sacré P.-Y., Coïc L., De Bleye C., Dumont E., Bouklouze A., Hubert Ph., Marini R., Ziemons E., Talanta, 207 (2020) 120306
[4] Coic L., Sacré P.-Y., Dispas A., Dumont E., Horne J., De Bleye C., Fillet M., Hubert Ph., Ziemons E., Talanta, 214 (2020) 120888
[5] Waffo Tchounga C., Sacre P.-Y., Ciza P., Ngono R., Ziemons E., Hubert Ph., Marini R., Joournal of Pharmaceutical and Biomedical Analysis, 194 (2021), 113761

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Technical Innovations and Clinical Translation in Raman Spectroscopy

Abstract

Raman spectroscopy offers label-free and non-invasive molecular information from biological samples and has shown vast potential for diagnostic applications. Nevertheless, the road for a clinical translation is full of technological and regulatory challenges. On the technical side, current fiber-based implementations of RS render imaging-acquisition impossible. Furthermore, single modalities provide a loop-sided picture of a disease, and the combination of multiple optical modalities is more promising. Regulatory challenges for in vivo applications in Europe include the new medical device regulation (MDR2017/745) for clinical investigations. Here, we present some recent developments in fiber-based imaging, multimodal instrumentation, and clinical translation of Raman spectroscopy. For example, we have developed a Raman-probe based imaging approach, using traditional fiber-optical probes in combination with real-time image and data-processing, which allows a real-time visualization of molecular information on a computer screen or directly on the sample surface, creating an augmented or mixed molecular reality image of the sample. Moreover, we have developed a combined RS, optical coherence tomography, and fluorescence life imaging microscopy for ex vivo tumor characterization. Because the signals are precisely co-registered with each other and with closely sampled H&E slides of entire biopsies, it is possible to intercorrelate the multimodal information at any location and assess the ground truth information. And at last, we present a RS-based system for in vivo endoscopy, which adheres to the high regulatory standard set-out by the MDR. The developed device is based on a 785 nm excitation and includes an in-house built fiber-optic Raman probe, which is developed in a single-unit and suitable for endoscopic in vivo investigations.

References

[1] Placzek F., E. Cordero, L. Wurster, Knorr, F., S. Kretschmer, Gerardo González-Cerdas G., Erkkilä M. T., Stein, P. Ataman, Hermann, G. G., Mogensen K., Hasselager T., Andersen P. E., Zappe H., Drexler W., Leitgeb R., Popp J., and Schie, I.W; Analyst, 2020
[2] Iwan W. Schie, Fabian Placzek, …., Wolfgang Drexler, Jürgen Popp & Rainer A. Leitgeb, Scientific Reports (2021), volume 11, Article number: 9951 (
[3] Eliana Cordero, Jan Rüger, Dominik Marti, Abdullah S. Mondol, Thomas Hasselager, Karin Mogensen, Gregers G. Hermann, Jürgen Popp, Iwan W. Schie, Journal of Biophotonics. 2019;
[4] Yang, W., Knorr, F., Latka, I., Vogt, M., Hofmann, G. O., Popp, J., & Schie, I. W., Light: Science & Applications (2022), 11(1), 1-12.
[5] David Vasquez, Florian Knorr, Franziska Hoffmann, Günther Ernst, Laura Marcu, Michael Schmitt, Orlando Guntinas-Lichius, Jürgen Popp, and Iwan W. Schie*, Analytical Chemistry 93, no. 33: 11479-11487; 2021.

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Interfacial Instability in Operating Lithium-Ion Batteries Unraveled by SHINERS

The fundamental understanding of the electrode/electrolyte interfacial processes in lithium-sodium ion batteries (LIBs) and of their dynamics upon cycling is of prime importance for the development of new generation electrode materials. Operando analyses using the utmost sensitive techniques are required to produce an accurate depiction of the underlying processes at the origin of the battery performance decay. If enhanced Raman Spectroscopy through the use of signal nano-amplifiers (SHINs) shows the required sensitivity [1,2,3,4], its implementation in operando conditions and particularly on functional materials in contact with organic electrolytes remains challenging. Through extensive optimization of SHINERS conditions for operando diagnosis of LIB materials, including the design of near-infrared active amplifiers and the control of the photon dose, the dynamics of interfacial composition upon cycling of various electrode materials in LIB coin-cells can be extracted. Interfacial instability unraveled on both negative (Solid Electrolyte Interphase: SEI) and positive (Cathode Electrolyte interface: CEI) electrodes can be tamed through fine tuning of the electrolyte composition.

References

[1] S. Hy, Felix; Y.-H. Chen, J. Liu, J. Rick, B.-J. Hwang "*In Situ Surface Enhanced Raman Spectroscopic Studies of Solid Electrolyte Interphase Formation in Lithium Ion Battery Electrodes*", J. Power Sources, 256 (2014) 324

[2] L. Cabo-Fernandez, D. Bresser, F. Braga, S. Passerini, L. J. Hardwick, "*In-Situ Electrochemical SHINERS Investigation of SEI Composition on Carbon-Coated* $Zn_{0.9}Fe_{0.1}O$ *Anode for Lithium-Ion Batteries*". Batter. Supercaps, 2 (2019) 168

[3] C.-Y. Li, Y. Yu, C. Wang, Y. Zhang, S.-Y. Zheng, J.-F. Li, F. Maglia, R. Jung, Z.-Q. Tian, Y. Shao-Horn, "*Surface Changes of* $LiNi_xMn_yCo_{1-x-y}O_2$ *in Li-Ion Batteries Using in Situ Surface-Enhanced Raman Spectroscopy*". J. Phys. Chem. C, 124 (2020) 4024

[4] A. Gajan, C. Lecourt, B.E. Torres Bautista, L. Fillaud, J. Demeaux, I.T. Lucas, "*Solid Electrolyte Interphase Instability in Operating Lithium-Ion Batteries Unraveled by Enhanced-Raman Spectroscopy*" ACS Energy Lett., 6 (2021) 1757

Figures

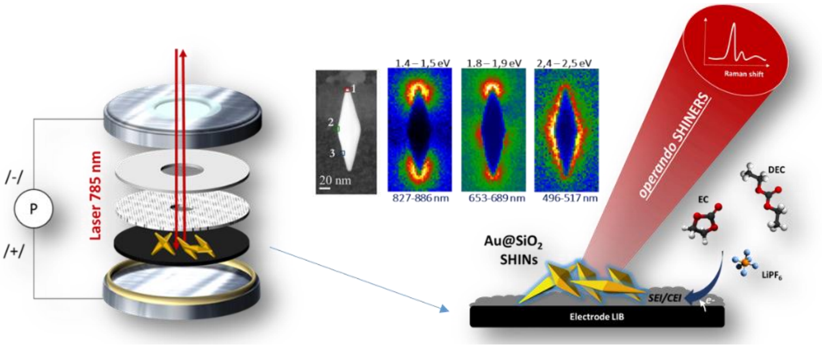

Figure 1: Operando SHINERS - Coin-cell Li-ion battery with SHIN-decorated electrode for operando diagnosis. SEI/CEI passive layer formation can be tracked operando using anisotropic SHINs ($Au@SiO_2$ core-shell bipyramid nanoparticles) combined with near-infrared Raman probe.

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SERS and molecular seed amplification to make diagnosis of Alzheimer’s disease

Alzheimer’s disease (AD) is the most common neurodegenerative disorder in the elderly with an incidence that progressively increases worldwide. One of the main neurological hallmarks of AD is the presence of amyloid-β protein (Aβ) aggregates which forms extracellular plaques in the neurons. At present, clinical diagnosis of AD relies on criteria that permit to classify the disease as possible or probable and a definitive diagnosis of AD can be done only *post-mortem* through neuropathological examinations [1].

In this work, we present an innovative approach in which a seed amplification assay (SAA) capable to detect traces of pathological Aβ species in the cerebrospinal fluid (CSF) is combined with Surface Enhanced Raman Spectroscopy for the ultrasensitive analysis of CSF collected from extensively-characterized patients with AD [2,3]. An optimized and low-cost silver nanowires/PTFE SERS-active substrate is employed for the sensitive and reliable spectroscopical analysis of the CSF amplified samples, with the support of a machine learning algorithm for the classification of the patients.

Our findings show that the SERS analysis performed on SAA end products could reveal chemo-structural information useful to distinguish AD from other neurological impairments in living patients and these results well correlated with the other clinical, instrumental and laboratory findings.

References

[1] Albert, M. S. et al., Alzheimer’s Dement., 7 (2011) 270.
[2] Bistaffa, E. et al., Brain Sci., 10 (2020) 815.
[3] Banchelli, M. et al., RSC Advances, 10 (2020) 21907.
[4] Barucci, A. et al., Analyst, 146 (2021) 674.

Acknowledgments

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SERS-based study supported by chemometric methods for the differential diagnosis of vaginal infections

Vaginal infections (vaginitis) are among the most common and problematic disorders that affect almost 70% of women during their whole lifetime at least once – the most prevalent are bacterial vaginosis (BV) and vulvovaginal candidiasis (VVC). Vaginitis is associated with the feeling of discomfort and can cause many severe diseases and complications *e.g.* premature rupture of membranes. The accurate diagnosis and implementation of appropriate medicines is an inherent element in successful treatment and provides protection against recurrence of infection. The whole situation is complicated by the fact that vaginal discharge may be altered due to physiological and pathological conditions such as desquamative inflammatory vaginitis (DIV), vulval dermatoses, or allergic irritation - not caused by biological agents. All this makes the differential diagnosis of vaginal infections of the utmost [1][2]. Surface-Enhanced Raman Spectroscopy (SERS) is based on the inelastic scattering of incident light by molecules adsorbed onto a roughened metal substrate (SERS substrate). SERS has been proved as a beneficial method due to its ultra-sensitivity and non-destructive nature that reveals specific fingerprint-like information down to the molecular level. This technique was utilized to study many biological systems such as: human tissues, cells, body fluids [3]. In this study for the first time, we used SERS and chemometric method - Partial Least Squares Regression (PLSR) to track the spectral response of vaginal fluids caused by different types of infections. We proved that the biochemical alterations that result from infections can be translated into a specific spectral image that is unique for each infection and hence their differentiation is possible at high level of explained information by PLSR. The integration of SERS-based sensors with a small, portable Raman spectrometer leads to the development of a handheld point-of-care device.

References

[1] Palmeira-de-Oliveira, R., Palmeira-de-Oliveira, A. Martinez-de-Oliveira, J., Advanced Drug Delivery Reviews, 92 (2015) 105–122
[2] Gutman, R. E., Peipert, J. F., Weitzen, S., Blume, J. Obstetrics and Gynecology, 3 (2005) 551–556
[3] Prochazka M, Bioanalytical, Biomolecular and Medical Applications, 1 (2016) 141-145

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A Fast Broadband Approach to the Analysis of Microplastics: Femtosecond Stimulated Raman Microscopy

Microplastics, mostly defined as plastic particles sized 1 µm to 5 mm, are emitted into the environment in large amounts [1]. They originate from the degradation of synthetic materials (secondary microplastics) or are produced intentionally (primary microplastics). The latter is often used in household products like cleaners or cosmetics. Raman microscopy is a commonly used method of analysis for microplastic contaminations [1]. It offers the possibility of accessing both quantitative information on the number, shape and size as well as chemical compositions of the contaminating particles. However, conventional Raman microscopy suffers from the usually low Raman scattering cross section of samples, resulting in a long acquisition time, and also from interfering fluorescent background. Therefore, the potential of non-linear Raman techniques such as CARS [2] and SRS [3] for the analysis of microplastics is currently investigated. Both techniques show some drawbacks for example in terms of a non-resonant background or incompleteness of spectra, respectively. Here, Raman imaging of microplastics by Femtosecond Stimulated Raman Microscopy (FSRM) will be reported for the first time. FSRM [4,5] yields complete Raman spectra with minimal acquisition times as short as 0.1 ms without distortions by fluorescence or a non-resonant background. In our proof-of-concept experiment, a microplastic particle in a commercial facial scrub is imaged (Figure 1). The image reveals the irregular shape of the particle which presumably enhances its exfoliating properties.

References

[1] Ivleva N.P., Chemical Reviews, 121 (2021) 11886
[2] Cole M., Lindeque P., Fileman E., Halsband C., Goodhead R., Moger J., Galloway T.S., Environmental Science & Technology, 47 (2013) 6646
[3] Zada L., Leslie H.A., Vethaak A.D., Tinnevelt G.H., Jansen J.J., de Boer J.F., Ariese F., Journal of Raman spectroscopy, 49 (2018) 1136
[4] Ploetz E., Laimgruber S., Berner S., Zinth W., Gilch P., Applied Physics B, 87 (2007) 389
[5] Czerwinski L., Nixdorf J., Di Florio G., Gilch P., Optics Letters, 41 (2016) 3021

Figures

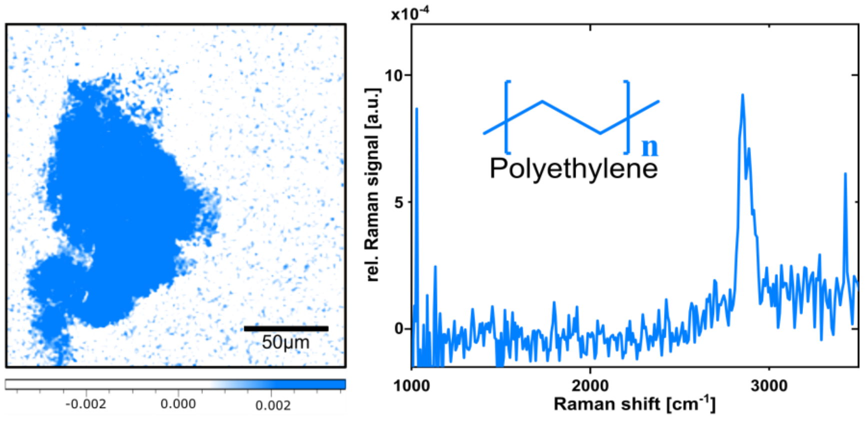

Figure 1: A chemical image of a polyethylene particle in a commercial facial scrub. In the Raman image at the left the FSRM signal at 2849 cm^{-1} is color-coded. Acquisition of the 200x200 µm image with a spatial resolution of 0.5 µm takes approximately 49 minutes. On the right, a single Raman spectrum from the chemical map is shown.

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High-speed Multicolor Stimulated Raman Imaging Enabled by a Compact and Robust Light Source

We present our recent developments in utilizing a compact and portable light source for high-speed multicolor stimulated Raman scattering imaging (SRS) in biomedical and medical environments.

For visualizing cells and tissue in SRS with high chemical specificity, successive images at multiple vibrational resonances must be acquired at video-rate speed. Recent approaches to video-rate multicolor SRS, based on parallel laser amplifiers or spectral focusing techniques [1,2,3], indeed allowed wavelength switching on a timescale of (sub)milliseconds, but restricted the tuning-bandwidth to below 300 cm^{-1} at maximum, significantly limiting the chemical specificity. In contrast, the here presented all-fiber light source is tunable within milliseconds across the broad spectral range between 700 and 3300 cm^{-1}, spanning the fingerprint, silent and high-wavenumber regions. To demonstrate the capabilities of the light source, it was applied in a proof-of-principle experiment for the differentiation of lipids and deuterated components with video-rate multicolor SRS imaging [4]. Successive images of the same sample were acquired with an acquisition time of 125 ms for each image (pixel dwell time of 750 ns, 100 x 100 pixel), limited only by the scanning speed and the sampling rate of the used home-built microscope. The excitation was switched in a frame-by-frame manner between 2150 and 2850 cm^{-1} in only milliseconds, a negligible time span compared to the acquisition time. As a result, a multicolor video of the sample with a frame rate of 8 Hz, i.e., a sub-framerate of 4 Hz for each wavenumber was recorded. Differentiating lipids and deuterated components with high specificity is a key requirement of several biomedical investigations, such as drug screening or imaging of metabolic changes in organisms and has not been shown with video-rate speed before. In order to evaluate the performance of the presented system for organism study, it was recently used by Hongli Ni et al. to image C.elegans in both fingerprint and C-H region [5]. Three characteristic vibrations were imaged for a quantitative analysis of the organism’s lipid metabolism: the 1650 cm^{-1} vibration (acyl C=C bond) shows the distribution of unsaturated fatty acids; the 1670 cm^{-1} vibration (sterol C=C bond) shows cholesterol distribution; the 2845 cm^{-1} vibration in the C-H region shows the overall lipid storage. Furthermore, by implementing active monitoring and closed-loop regulators, we have achieved long-term power stability with a standard deviation of less than 0.3 % and wavelength stability better than 5 pm throughout 100 h. These developments constitute necessary steps for advancing SRS imaging in terms of reliability, ease-of-use, and specificity for applications in biomedical and medical environments.

References

[1] S. Heuke, B. Sarri, X. Audier, and H. Rigneault, Opt. Lett., 43 (2018), 3582-3585.
[2] Y. Ozeki, T. Asai, J. Shou and H. Yoshimi, IEEE Journal of Selected Topics in Quantum Electronics 25 (2019), 1-11.
[3] M. Alshaykh, C. Liao, O. Sandoval, G. Gitzinger, N. Forget, D. Leaird, J. Cheng, A. Weiner, Opt. Lett. 42 (2017), 1548–1551.
[4] T. Würthwein, K. Wallmeier, M. Brinkmann, T. Hellwig, N. M. Lüpken, N. S. Lemberger, and C. Fallnich, Biomed. Opt. Express 12 (2021), 6228-6236.
[5] H. Ni, P. Lin, Y. Zhu, M. Zhang, Y. Tan, Y. Zhan, Z. Wang, and J. Cheng, Analytical Chemistry 93 (2021), 15703-15711.

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Defects in polymer multilayer films: A new way to investigate based on Raman microscopy

Polymer multilayer films are presents everywhere in our world. Thus, we can find them in food packaging, on car coatings, in phone protection films, among many other applications. But their characteristics are questioning as soon as a defect is present. Unfortunately, it's not easy to locate this defect, and consequently chemically characterize and identify it.

Confocal Raman microscopy is a perfect candidate for such issue, combining the high spatial resolution of optical microscopy with the chemical identification through the spectral characterization.

This combination makes our Raman confocal microscope the ideal solution for non-destructive highly resolved characterization of the defect realizing a very fast survey mapping of the sample.

Figures

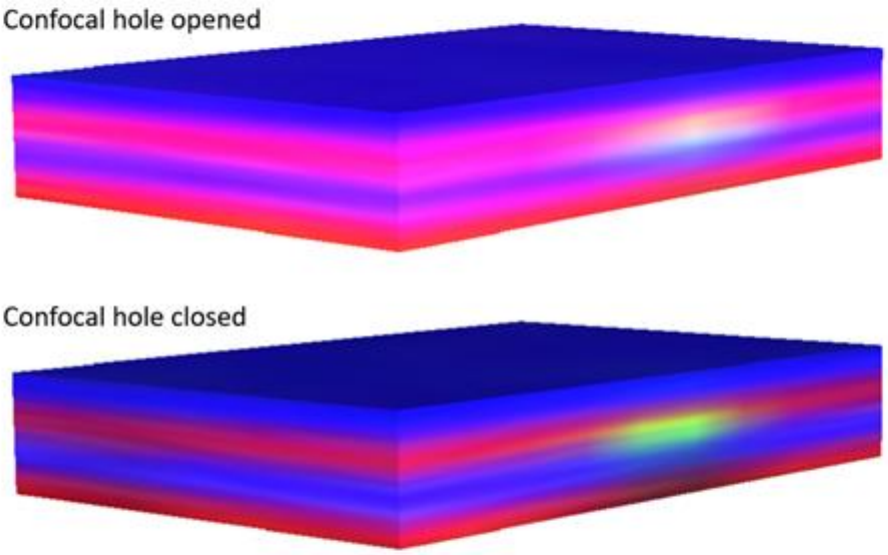

Figure 1: 3D Raman map of an feature in a multilayer polymer sample. The colors represents the different chemical fingerprint. Blue: Plastic tape. Red: Glue. Green: Feature. Map dimension: 500x500x100µm with 50x50x1µm steps. (Top) Map with confocal hole opened. (Bottom) Map with confocal hole closed.

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Life Science in Live by Nonlinear Microscope and Endoscope

Nonlinear imaging techniques, such as 2-photon/3-photon autofluorescence, second/third harmonic generation (SHG/THG), coherent anti-Stokes Raman (CARS) scattering and stimulated Raman scattering (SRS), stand out for life science applications by their label-free property. These techniques can be used to observe morphology of biological systems or targeting specific molecules in the system. Together with a fast-scanning system, nonlinear techniques can be also used to follow real-time dynamic biological process, such as animal metabolic process, molecular delivery in skin and neural activities in brain.

We developed a fast, sensitive and compact nonlinear microscope system, which includes 2-photon fluorescence, SHG and SRS imaging. Our microscope has been used for medical applications (tumor diagnose [1], organoid observation), chemical and pharmaceutical applications (cosmetic spreading, pharmaceutical tablet quality control [2]) and biological applications (metabolic process [3], molecular penetration in skin[4]).

To go one step further, we also integrate nonlinear techniques (2-photon/3-photon, SHG/THG, CARS) in a flexible endoscope (see Figure 1) [5], to access samples that cannot be placed in a microscope, and to observe biological process in a living model such as mice [6].

In conclusion, our nonlinear microscope and endoscope can provide label-free live imaging for various biological and biomedical applications and can be adapted for different samples *in vitro* and *in vivo*.

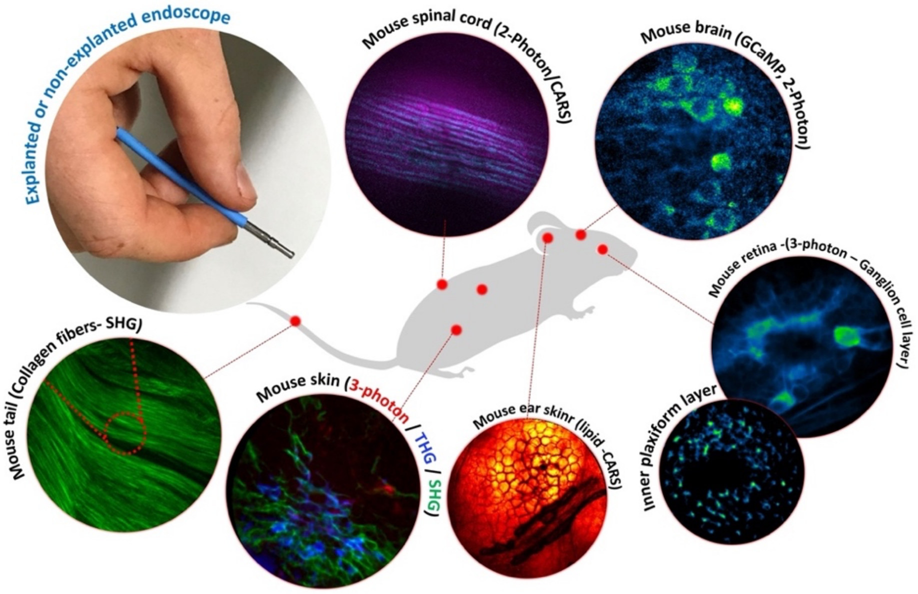

Figure 1: Imaging different locations on/in mice using nonlinear endoscope M-FIP.

References

[1] B. Sarri, et al., Biomed. Opt. Express, 10(2019) 5378-5384
[2] B. Sarri, et al., Journal of Raman Spectroscopy, 50 (2019) 1896-1904
[3] S. Heuke, et al., Biomed. Opt. Express, 12 (2021) 7780-7789
[4] X. Chen, et al., J. of Controlled Release, 200 (2015) 78-86
[5] A. Lombardini, et al.,Light : Science & Applications 7(2018) 10
[6] D. Septier, et al., Optics Express, 30(2022) 25020-25033

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Multivariate Statistics methods for cancer grading

Abstract

In the last decade, Raman Spectroscopy has demonstrated to be a label-free and destructive optical spectroscopy able to improve diagnostic accuracy in cancer diagnosis [1]. This ability is principally based on the great amount of biochemical information dealt out by the Raman scattering with biological tissues under investigation. However, to achieve clinical requirements, the spectroscopic analysis and its ability of grading cancer tissues require sophisticated multivariate statistics [2-3]. In this presentation, we critically review multivariate statistics methods analyzed at the light of their ability to process datasets generated by Raman spectroscopy on chondrogenic tumors where distinguishing between enchondroma and first grade of malignancy is a critical problem for pathologists.

References

[1] D’Acunto, M.; Gaeta, R, Capanna, R.; Franchi, A. Contribution of Raman Spectroscopy to Diagnosis and Grading of Chondrogenic Tumors. *Sci. Rep.* (2020), *10*, 2155. 35

[2] 2. Lui, H.; Zhao, J.; McLean, D.; Zeng, H. Real-time Spectroscopy for *in Vivo* Skin Cancer Diagnosis. *Canc. Res.* (2012), 72, 36 2491-2500. 37

[3] 3. Davis, L.E.; Shalin, S.C.; Tackett, A.J. Current state of melanoma diagnosis and treatment. *Canc. Biol. Ther.*(2019), *20*, 1366-1379.

Figures

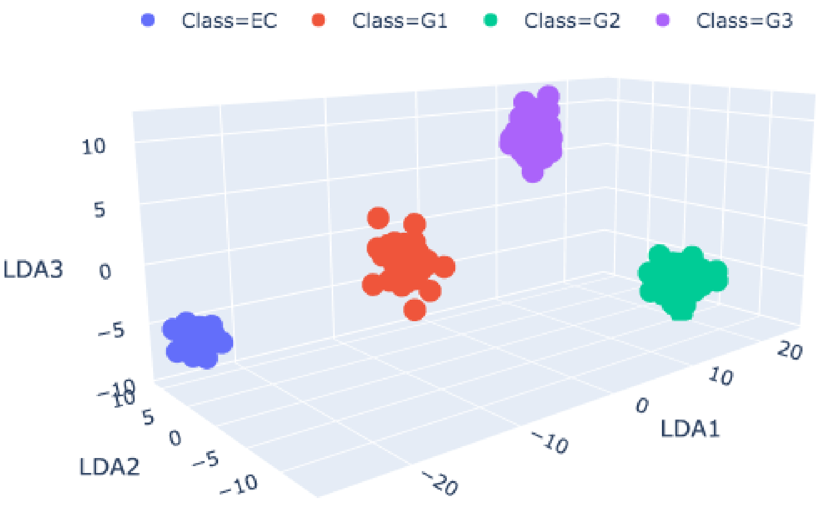

Figure 1: 3D representation of Linear Discriminant Anansyis component for the four Chondosarcoma malignancy groups.

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Widely-tunable, doubly-resonant Raman scattering on diamond in an open microcavity

Raman lasers are a valuable resource for frequency conversion of coherent light. Diamond, in particular, is a material well-suited for Raman lasers due to the wide transparency window, high thermal conductivity and a large Raman gain. The implementation of a low-threshold Raman laser in the visible, however, remains elusive due to material and fabrication limitations. Nevertheless, nanophotonic engineering offers a viable route to reduce the pump-power threshold.

Open microcavities have emerged as versatile platform for enhancing light-matter interactions on the account of full *in situ* tunability. These cavities offer the possibility to incorporate micron-sized crystalline membranes [1], while maintaining an appreciable ratio of quality-factor to mode volume [2]. In this work, we propose to use a diamond micromembrane embedded in such an open microcavities as a novel platform for the realization of a low-threshold Raman laser [3]. We characterize the performance of the cavity and demonstrate quality-factors exceeding 100 000. We next establish a configuration with the pump laser and the Raman transition simultaneously resonant. We further demonstrate a >THz continuous tuning range of this doubly-resonant Raman scattering condition by exploiting the *in situ* tuning capability of our platform. We predict that the current platform can achieve Raman lasing in the visible with mw pump-threshold powers. Our results are generic and applies to other solid-state materials given that a high-quality membrane can be fabricated, thus paving the way for the creation of a universal low-power frequency shifter; a valuable addition to the nonlinear optics toolbox.

References

[1] D. Riedel, S. Flågan, P. Maletinsky, & R. J. Warburton, Phys. Rev. Applied **13**, 014036 (2020).
[2] S. Flågan, D. Riedel, A.Javadi, T.Jakubczyk, P. Maletinsky, & R. J Warburton, J. Appl. Phys, **131** 113102 (2022).
[3] S. Flågan, P. Maletinsky, R. J. Warburton & D. Riedel, arXiv:2110.06242 (2021).

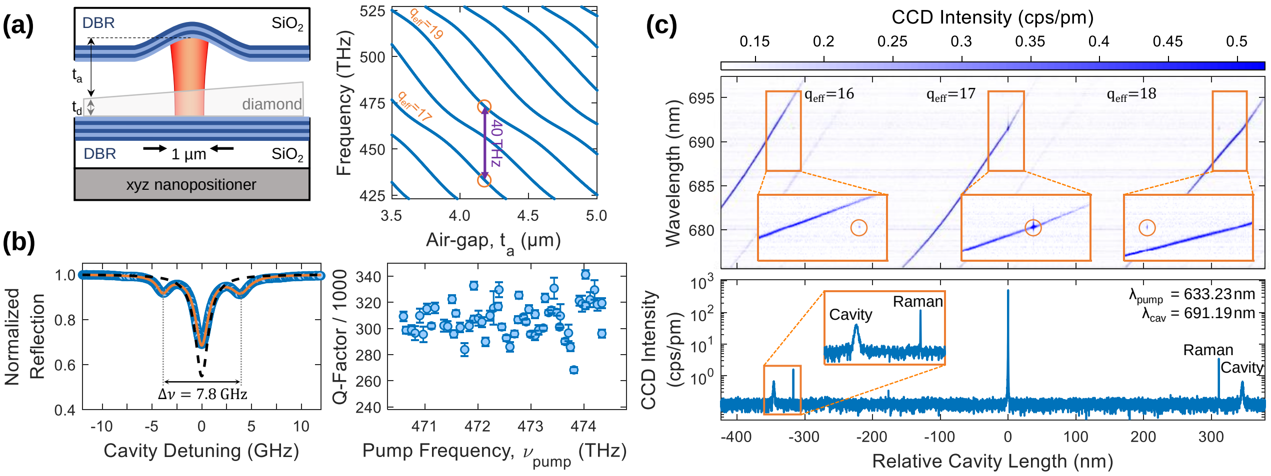

Figure 1: (a) Tunable cavity platform (left) and typical mode structure (right). (b) Characterization of the cavity performance. (c) Demonstration of the doubly-resonant configuration, with the pump laser and Raman simultaneously resonant.

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Silica Coated Gold Nanorod Supraparticles: a Tunable Platform for Surface Enhanced Raman Spectroscopy

Gold nanorod (AuNR) based assemblies are promising functional materials for Surface Enhanced Raman Spectroscopy (SERS) due to the shape induced tunable localized surface plasmon resonance (LSPR) of AuNRs. Designing the optimal assembly structure for SERS, however, is challenging and requires a delicate balance between the interparticle distance, porosity and wetting of the assembly. Here, we introduce a new platform of AuNR assemblies for sensing utilizing their collective ensemble properties. Our design relies on a solvent evaporation approach to assemble silica coated gold nanorods (Au@SiO_2 NRs) dispersed in emulsion droplets into spherical supraparticles in which the thickness and porosity of the silica shell are exploited to control the plasmonic coupling between the AuNRs and the mass-transport through the supraparticle, respectively. Moreover, etching the AuNRs inside their mesoporous silica shells allows fine-tuning of the plasmonic response to the laser excitation wavelength. The SERS performance of various supraparticles was investigated as a function of the assembly porosity, interparticle distance, and LSPR of the AuNRs using a novel correlative SERS-electron microscopy approach. Altogether, the Au@SiO_2 NR supraparticles introduced in this work present a novel class of materials for sensing, and opens up a wide parameter space to optimize performance and use in heterogeneous catalysis.

References

[1] J. E. S. van der Hoeven, H. Gurunarayanan, M. Bransen, D. A. Matthijs de Winter, P. E. de Jongh, A. van Blaaderen, Adv. Funct. Mater., 2022, 22001458
[2] J. E. S. van der Hoeven, T. S. Deng, W. Albrecht, L. A. Olthof, M. A. van Huis, P. E. de Jongh, A. van Blaaderen, ACS Omega, 2021, 7034
[3] T. S. Deng, J. E. S. van der Hoeven, A. O. Yalcin, H. W. Zandbergen, M. A. van Huis, A. van Blaaderen, Chem. Mater., 2015, 7196

Figures

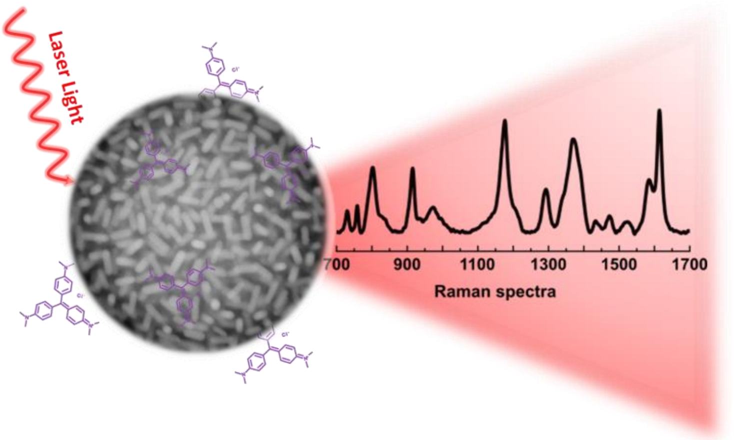

Figure 1: Silica coated Au nanorod supraparticles for SERS

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Raman study of the as-prepared and flash-lamp annealed thin films of Cu_2ZnSnS_4 nanocrystals mixed with PEDOT:PSS

New materials for future of renewable energy, especially photovoltaics, should be cheap, environmentally friendly and have a direct bandgap, which ensures sufficient absorption in the entire solar spectrum. However, absorption of light is usually also accompanied by additional heating of the device. This heat can be either wasted or transformed into extra electrical energy. That is why materials that allow photovoltaics to be combined with thermoelectrics are gaining popularity. One of the materials that are attracting the attention of researchers in this respect is Cu_2ZnSnS_4 (CZTS). It has nontoxic and relatively cheap constituents as well as promising photovoltaic and thermoelectrical properties. CZTS can be produced by a variety of techniques, including low-temperature colloidal synthesis in aqueous solutions. This "green" chemistry approach makes it an even more attractive candidate for future applications in novel renewable energy devices. However, due to the complex structure of CZTS, there are several structural modifications, and a high probability of the formation of antisite Cu_{Zn} and Zn_{Cu} defects as well as secondary phases in the form of binary and ternary compounds from constituent elements. By varying the nanocrystal (NC) synthesis parameters and the conditions of NC film deposition, the formation of secondary phases and antisite defects can be suppressed. Another widely used material in both photovoltaic and thermoelectrical applications is the p-type conductive polymer PEDOT:PSS. In some works CZTS NCs and PEDOT:PSS were used as parts of the same device structure but as separate layers with different functional roles in the device. On the other hand, incorporation of CZTS NCs into a PEDOT:PSS matrix can be a promising approach, since as shown in the literature [1–3] for other nanoparticles adding them to PEDOT:PSS may improve its thermoelectric properties. Another perspective of the CZTS NC-PEDOT:PSS composite is the combination of the excellent properties of CZTS as an absorber of solar radiation and the high electrical conductivity of PEDOT:PSS. This approach could solve the problem of poor electrical transport between NCs, which is the main obstacle on the way towards potential applications of any kind of NC thin film. Not only the NC synthesis and the thin film preparation conditions but also post-synthesis processing of the NC films is important to improve the functional properties of the NC films. In terms of scalability and processing time, flash lamp annealing (FLA) technique (also known as intense pulse light (IPL) annealing) is an interesting alternative to furnace annealing. This technique is known for over 50 years, but began to gain popularity just for the last few years with the technology transition towards thin-film roll-to-roll manufacturing. Raman spectroscopy is a very powerful tool for CZTS NCs characterization. It allows not only the presence of possible secondary phases to be determined, but also structural modification of CZTS NCs to be identified. Here we present results of a Raman spectroscopy study of CZTS/PEDOT:PSS composite films, prepared from aqueous colloidal solution of CZTS NCs mixed in different proportions with PEDOT:PSS solution and deposited onto glass substrates. The parameters of the film deposition were optimized to avoid aggregation of the NCs and formation of secondary phases in them. Subsequently, the composite films were subjected to FLA treatment. To the best of the authors' knowledge, this is the first study of FLA treatment of PEDOT:PSS and CZTS NCs in PEDOT:PSS matrix. It was revealed, that even small concentrations of PEDOT:PSS in mixed composites lead to the formation of optically more homogeneous films. Moreover, the FLA treatment increases the stability and improves the crystallinity of CZTS NCs with simultaneous decomposition of PEDOT:PSS.

[1] A. Gamal El-Shamy, *Chem. Eng. J.*, 417 (2021), 129212.
[2] F. P. Du, N. N. Cao, Y. F. Zhang, et al., *Sci. Rep.*, 8 (2018), 1–12.
[3] S. Shisodia, B. Duponchel, G. Leroy, et al., *Sustain. Energy Fuels*, (2022), DOI:10.1039/D2SE00403H.

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Enhanced Tri-modal Optical-Photothermal Infrared (O-PTIR) Spectroscopy – Advances in Spatial Resolution, Sensitivity & Tri-modality (IR, Raman & Fluorescence)

Optical Photothermal Infrared (O-PTIR) spectroscopy has established itself as a cutting edge vibrational microspectroscopy tool, offering significant advantages over the traditional FTIR/QCL & Raman spectroscopic tools, providing submicron simultaneous IR+Raman microscopy, in non-contact mode with high sensitivity. The ability to collect, for the first-time submicron IR spectroscopic data in an optical microscope has enabled new research outcomes across a range of application fields, such as life sciences (cells, tissues, bacteria), polymers, cultural heritage and microplastics.

A new modality, “counter-propagating” has been engineered to provide for enhanced IR (and Raman) spatial resolution and sensitivity, through decoupling the need for a reflective objective. The IR pump beam can now be directed to the sample via the underside, thus allowing the collection objective for the visible probe (and Raman excitation beam) to be a high-NA refractive objective. This improves spatial resolution to ~300nm for both IR and Raman, whilst improving sensitivity, image quality and facilitating immersion objective studies.

To further integrate vibrational spectroscopic tools into life science workflows, we coupled widefield epifluorescence to facilitate a novel concept – fluorescence guided (or fluorescence co-located) O-PTIR microspectroscopy. Rather than, or in addition to the visible image, the fluorescence image can now be used to guide the user to the region of interest, thus combining the well-established specificity of fluorescence imaging with the broad macromolecular profiling capabilities of IR spectroscopy

Several life sciences examples from bacteria, cells and tissues will be provided to demonstrate these new capabilities and how they can enable new experiments and research findings..

Figures

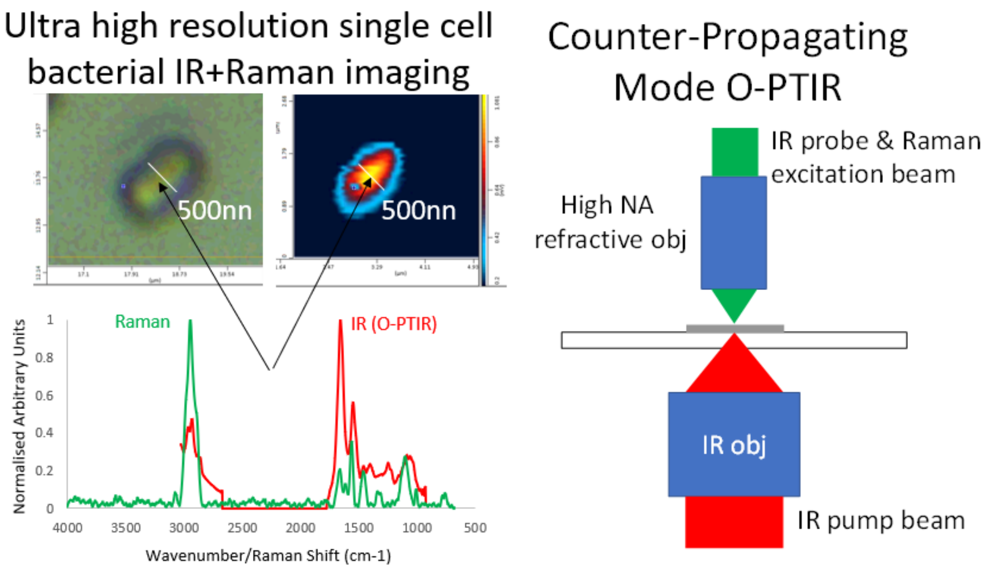

Figure 1: Left: Single E.Coli cell imaged in counter-propagating mode with 50nm pixel/step size and submicron simultaneous IR+Raman spectra from centre of bacterial cell. Right: Schematic of counter-propagating layout.

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Short peptide, thin layers and the perspective of their use in SERS-based sensors

Protein-mediated processes occurring in complex biological environments involve specific interactions under strictly defined conditions. Protein-derived peptides constitute a large group of biomolecular receptors with the remarkable ability to recognize various molecules and respond through a conformational transition to external stimuli such as local pH or the presence of biologically relevant cations. Coupling of such biology-inspired receptors to plasmonic nanostructures opens a new and fascinating route for creation of sensitive and selective nanosensors utilizing surface-enhanced Raman scattering (SERS) effect. In particular, short peptides are very attractive in this respect due to their bioactivity and the ease with which their structural and functional responses may be tuned according to environmental conditions. This underlies the design flexibility of SERS-based sensors employing peptide-derived receptors.

Design of such sensors requires a deepened understanding of the dynamic structural and physicochemical properties of peptide layers in response to external stimuli. We propose that conformationally labile peptides firmly attached to plasmonic substrate by cysteine (Cys) residue and containing a tryptophan (Trp) Raman probe can be employed as SERS-based sensors to detect for example local pH or concentration of certain biologically relevant ions.

We took the first step to achieve this goal by a comprehensive SERS study of short peptides comprising cysteine and/or tryptophan units. We investigated effects of terminal modifications and the amino acid sequence order in dipeptides composed of Trp and Cys on their SERS signals [1], the accessibility of both thiol moieties to interact with Ag nanoparticles for rigid cyclo(L-Cys-D-Cys) (diCys) structure, and suitability of isotopically labeled Cys (^{13}C and ^{15}N) to improve analysis of vibrational signatures within SERS response [2]. We demonstrated that the SERS spectra of dipeptides consisting of Trp and Cys residues were strongly dominated with the bands due to the vibrations of the Trp moiety. The SERS response was only slightly affected by the peptide sequence and terminal modifications under the fixed experimental conditions; however these two parameters became critical parameters when the effect of the substrate type and excitation wavelength is taken into consideration. We propose that the surface coverage of diCys on silver surface and thus the adsorption mode, which further affects the aggregation of Ag nanoparticles and the availability of the free thiol groups, can be guided by experimental conditions. On the other hand, the use of isotopically-labeled SERS allowed us to probe dynamics within the monolayer composed of L-cysteine and $^{13}C_3$ and ^{15}N L-Cys isotopologues, providing rare insights into murky phase transition unraveled only through this novel methodological approach [2].

Our initial findings allowed us to evaluate the efficiency of short peptide chemisorption and its SERS features, as well as showed the ability of tailoring the peptide adsorption properties with the experimental protocol. A potential of isotopically-edited SERS approach to gain deeper insights into relationship between local structure/conformation and SERS signals of the adsorbed peptide was demonstrated. All of these constitute a valuable introductory step to the informed selection of nature-inspired of stimuli-responsive peptide motifs for SERS nanobiosensors.

References

[1] A. Królikowska, J. Cukras, M. Witkowski, D. Tymecka, A. Hernik-Magoń, A. Misicka, W. Dzwolak, J. Phys. Chem. C, 124 (2020) 7097

[2] [1] M. Witkowski, A. Królikowska, J. Cukras, W. Dzwolak, ChemRxiv (2022), DOI: 10.26434/chemrxiv-2022-ql9f8

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Improving Nano-Biology Interaction Studies with Multi-Modal Raman & Enhanced Darkfield Optical Hyperspectral Microscopy

Effective studies at the nano-bio interface require that researchers can easily observe and measure how nanoparticles interact with a targeted in-vitro cell or ex-vivo tissue environment. HORIBA Scientific and CytoViva, Inc. now provide a new multi-modal Raman and enhanced darkfield hyperspectral microscopy system that is highly effective for nano-biology related research. This system includes patented enhanced darkfield optics that enable label-free observation of nanoparticles as small as 10nm when isolated in solution and in cells and tissue. The optical hyperspectral imaging capability enables rapid capture of large-area hyperspectral images for spectral characterization and spectral mapping of nanoparticles or their drug load. Pixel-level optical hyperspectral data is captured based on the nanoparticle's surface plasmon resonance, fluorescence emission or Rayleigh scatter. Additionally, Raman measurements from the identical field of view can be captured, which provides quantitative molecular fingerprint confirmation of the nanoparticles or other sample elements. Finally, Raman mapping of unique sample elements can also be performed when required. This presentation will provide a detailed overview of this new multi-modal imaging and spectral measurement capability. Specific illustrations of plasmonic, metal oxide, polymer and lipid-based nanoparticles interacting with cells and tissue will be presented.

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When Raman and friends go to the mountains – correlative analysis with MountainsSpectral®

Based on science's most trusted analysis software platform, MountainsSpectral® is a comprehensive, dedicated solution for processing & combining images and other data from spectroscopic techniques including Raman, TERS, IR, nanoIR, fluorescence, photoluminescence, cathodoluminescence, EDX/EDS and XPS as well as microscopy data.

In particular, it opens up new possibilities and workflows for the analysis of spectroscopic data including: spectral map processing and enhancement, colocalization for correlative analysis, topographic analysis tools for AFM images, SEM image 3D reconstruction, particle analysis and spectral analysis.

Figures

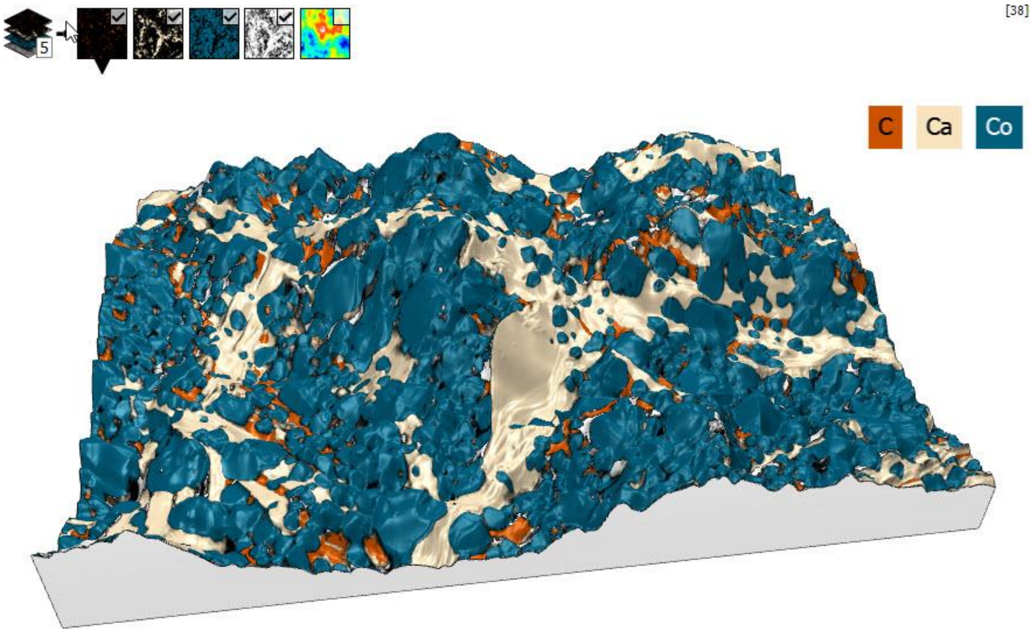

Figure 1: 3D model of surface topography generated from SEM images with overlay of chemical composition (EDS maps) on a Cobaltite sample.
Courtesy of Emmanuel Guilmeau, CRISMAT (Caen, France), Jean-Claude Ménard, JEOL France.

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Long Photo-Induced Enhanced Raman Scattering (PIERS) in Au nanoparticles embedded in TiO_2

Enhancing Raman scattering is known for more than 40 years now and has been thoroughly investigated. For this a nanostructured metallic substrate is required and it is commonly admitted that this so-called SERS effect can enhance the Raman intensity by a factor greater than 10^6 (depending on the substrate). Recently, it has been shown that it is possible to increase the enhancement even more if the metallic nanostructures are deposited on a semi-conducting surface and exposed to UV radiation prior to the detection [1]. A few tenth of paper have investigated this PIERS effect, however, none of them have succeeded in it making last more than an hour. In this presentation we will show that by co-depositing the Au nanoparticles together with the TiO2 matrix it is possible to prolongate the duration for at least 8 days. To understand further the specificity of our sample structuration, we have performed cathodoluminescence experiments. The results suggest that the exposition to UV irradiation leads to shorten the width of the Schottky barrier between Au and TiO_2 which is favorable to an enhancement of the chemical effect [2].

References

[1] S. Ben-Jaber, W. J. Peveler, R. Quesada-Cabrera, E. Cortés, C. Sotelo-Vazquez, N. Abdul-Karim, S. A. Maier, I. P. Parkin, Nat. Commun. 2016, 7, 12189.

[2] Andrea Brognara, Beatrice R. Bricchi, Ludovic William, Ovidiu Brinza, Maria Konstantakopoulou, Andrea Li Bassi, Matteo Ghidelli, and Nathalie Lidgi-Guigui, Small, 2022

Figures

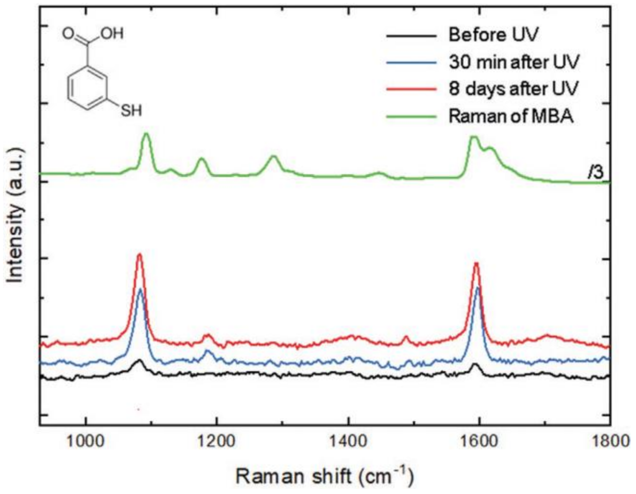

Figure 1: SERS spectra of Mercaptobenzoic Acid on Au nanoparticles embedded in TiO_2 before and after UV irradiation

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A Fibre-Packaged Waveguide-Enhanced Raman Sensor

Waveguide-enhanced Raman spectroscopy (WERS) has attracted significant interest as a method leveraging the performance, size, and cost benefits of integrated photonics for Raman spectroscopic sensing of chemical and biological species [1]. While all the components of a full WERS system (light source, filters, interaction region, spectrometer) may eventually be integrated on a single chip, current limitations mandate using a source and spectrometer that are off-chip. The coupling of light to and from the WERS chip is most practically done using optical fibres, which can be bonded to the chip to remove the vibration sensitivity and need for expensive alignment stages inherent to lens coupling. Fibre-coupling however requires additional components to avoid the background from the fibres, notably a coupler separating the forward- and backward-propagating signals [2].
We present a fibre-packaged waveguide-enhanced Raman spectroscopic sensor with an adiabatic directional coupler enabling the collection of the backscattered signal and the removal of any signal from the fibres. Its limit of detection was quantified by measuring varying concentrations of isopropyl alcohol (IPA) in water. The signal-to-noise ratio (SNR) was calculated for each spectrum by normalizing the spectrum, subtracting a reference measurement of deionized water, and applying a penalized least squares algorithm to remove the baseline [3]. A fit of the evolution of the SNR with concentration suggests that the sensor's LoD for IPA lies at 0.03 mol.L^{-1} (0.2 wt% in water). This LoD is the lowest reported to date for a WERS sensor without surface enhancing mechanism.

References

[1] M. Ettabib, A. Marti, Z. Liu, B. Bowden, M. Zervas, P. Bartlett, and J. Wilkinson, "Waveguide Enhanced Raman Spectroscopy for Biosensing: A Review", ACS Sensors, vol. 6, pp. 2025-2045, 2021.
[2] D. Kita, J. Michon, and J. Hu, “A packaged, fiber-coupled waveguide-enhanced Raman spectroscopic sensor,” Optics Express, vol. 28, pp. 14 963–14 972, 2020.
[3] J. Ye et al. “Baseline correction method based on improved asymmetrically reweighted penalized least squares for Raman spectrum”, Applied Optics, vol. 59, pp. 10933-10943, 2020.

Figures

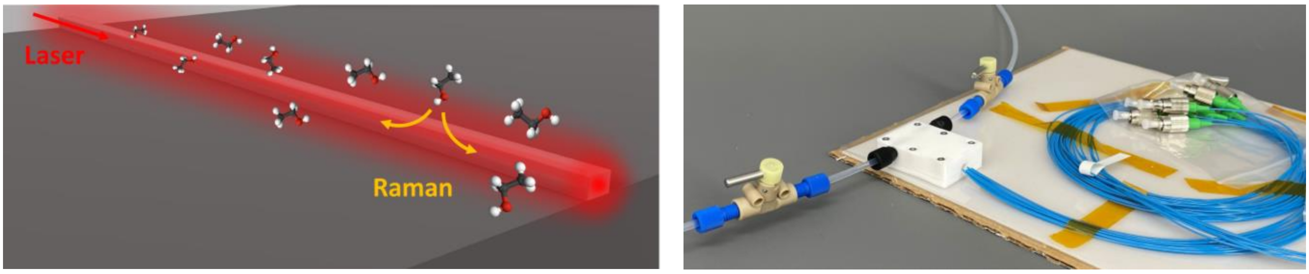

Figure: Schematic principle of WERS. A WERS sensor integrated in a flow cell for fluidic measurements.

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Studying 2D nanomaterials using Coherent Raman scattering (CARS): the example of Boron Nitride

Boron Nitride (BN) has attracted a lot of interest over the last years, being the counterpart to graphene, the ideal substrate that could preserve the high electron conductivity graphene has to offer. However, contrary to graphene, the lack of an accessible electronic resonance due to the large band gap (>6 eV) of BN makes its spontaneous Raman signal very weak. Mapping BN samples is thus cumbersome and time consuming, each pixel requiring few seconds of exposure time. New BN synthesis methods being such a burning research subject, removing the barriers for efficient characterization of BN appears crucial. Coherent Raman scattering (CRS) [1] techniques, such as coherent anti-Stokes Raman scattering (CARS), or stimulated Raman scattering (SRS) have been applied to many fields, ranging from life science, to solid state characterization. In the last decade, ultrashort laser pulses have been used to generate coherent processes, which greatly enhance the signal up to several order of magnitude. Although of limited interest for graphene [2], CRS appears to be an interesting candidate for 2D nanomaterial characterization when the spontaneous Raman is too weak. Still, research on the subject is scarce: Lafeta et al. [3] presented CARS spectra of hexagonal BN (h-BN), graphene and graphene/h-BN heterostructure, and Ling et al. [4] used SRS for rapid imaging and thickness measurements of h-BN flakes. Here, we present a work on rapid imaging of h-BN flakes using CARS microscopy. A fs/ps-CARS spectroscopy setup [5] was adapted to fit microscopy applications. Coherent Raman response of h-BN is obtained on tens of nanometers thick flakes, and compared it to the spontaneous Raman response. With similar band position and full width half-maximum, high signal enhancement is demonstrated. Thus, hyperspectral imaging of BN flakes is successfully performed within minutes, instead of hours (Figure 1). Thickness sensitivity could be obtained down to 11 nm, according to AFM measurements. This is very promising for fast characterization and quantification of thin h-BN with large spatial extent. Furthermore, this setup may also be well suited for fast detection and identification of other solid compounds. In particular, ongoing studies on simili-explosive species will be discussed in the context of threat prevention.

References

[1] D. Polli, V. Kumar, C. Valensise et al., Laser and Photonics Reviews, 12 (2018) 1800020
[2] A. Virga, C. Ferrante, G. Batignani, Nature Communications, 1 (2019) 1-9
[3] L. Lafetá, A. Cadore, T. Mendes-De-Sa et al., Nano Letters, 6 (2017) 3447-3451
[4] J. Ling, X. Miao, Y. Sun et al., ACS Nano, 12 (2019) 14033-14040
[5] R. Santagata, M. Scherman, M. Toubeix et al., Optics Express, 23 (2019) 32924

Figures

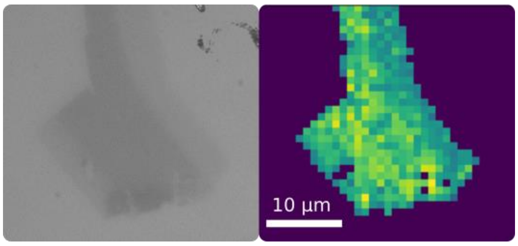

Figure 1: Side-by-side comparison of white light image and CARS hyperspectral reconstruction of an h-BN flake. Exposure time/pix = 100 ms.

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Analysis of micro and nano plastic particles on porous filter cascade systems

In the last years the research on micro and nanoplastic (NMP) particles in water and in air is growing very fast. Routines for analysis of microparticles in the range of 100 to 10 µm are very well stablished form particle analysis to mass spectroscopy [1]. Current efforts are focused in the submicrometer to nanometer range down to few tens of nanometer [2].

In this work we present an novel filtration system for micro and nanoparticles using a cascade stack with two different filter membrane. The frist filter with large pores (with diameter down to 1 µm) is produced by laser drilling or chemical etching. The second filter is fabricated by chemical etching of Al_2O_3 and can be used for filtration of particles down to few tens of nanometers [3]. The selectivity can be adjusted in principle trough the filter porosity. The main advantage of our filter system is the flexibility to be used by both scientific communities, first one working in mass spectrometry and the second one in particle analytics. Especially the second community is interested in the number of particles in size fractions, the overall size distribution as well as the chemical composition. Moreover, both materials, Si and Al_2O_3 are very well suited for many analytical NMP applications like µ-Raman spectroscopy, SEM AFM, AFM-Raman or other nanoanalytical instrumentations.

As an example, we present here the latest results on NMP particle identification using Raman spectroscopy of two model materials, PET and PS. PET reference NMP material is prepared by cryo milling with an average particle size of 22 µm, PS particles are monodisperse with mean diameter of 140 nm.

References

[1] Bauer, J., et al. (2019). Microplastic detection and analysis in water samples. IC SEWEN19, Quatar, Springer nature

[2] P.-T.Miclea, S. Richter, C. Hagendorf, Size-selective nano and micro plastic particle analysis on nano-porous membrane filter cascades, *Appl. Res.*, (2022), submitted

[3] SmartMembranes (2020). "SmartPor: Nanoporous Alumina." from http://www.smartmembranes.de/en/products/nanoporous-alumina/

Figures

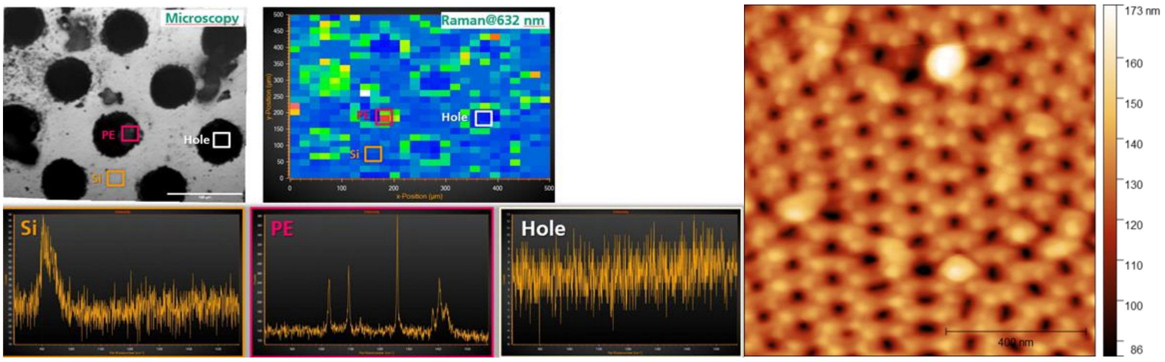

Figure 1: PE microparticles on Si Filter with pore size og 50 µm (left) and AFM image of PS and PE nanoparticles on Al2O3 Filter with pore size of 90 nm (right)

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Local Raman spectroscopic fingerprints of TMDC-metal interactions

Metal-mediated exfoliation of TMDCs has recently attracted considerable interest due to high yields of large size monolayer flakes [1]. The van der Waals interaction between metals and TMDCs enables the exfoliation of large size monolayers but also alters their properties due to strain and charge doping.
First, the exfoliation of large-area monolayers on different metals (Au, Ag, Pt, Pd, Cu, Ni, Co, Cr, and Ti) will be presented, where the nobility of the metal was correlated with the size of the exfoliated MoS_2 [2]. The oxidation levels were studied with XPS, while the effects of strain and charge doping are explained with Raman spectroscopy measurements.
In the second part an in-depth study of the strain and charge doping fingerprints of the strong interaction between monolayer MoS_2 and Au will be presented [3]. The interaction with different types of Au (e-beam evaporation, magnetron sputtering, thermal evaporation, single crystal Au (111)) was studied with AFM, Raman spectroscopy, TERS, and XPS. The strength and the heterogeneity of the MoS_2–Au interaction, strongly correlates with the Au roughness and was confirmed with nanoscale TERS mapping. The TMDC-Au interaction is also evidenced by the appearance of additional, otherwise forbidden Raman modes, and it can be modulated by the force set-point of the TERS tip [4].

References

[1] Velicky, M., Donnelly, G.E., Hendren, W.R., McFarland, S., Scullion, D., DeBenedetti, W.J., Correa, G.C., Han, Y., Wain, A.J., Hines, M.A. and Muller, D.A., ACS nano, 12, no. 10 (2018): 10463-10472.
[2] Velický, M., Donnelly, G.E., Hendren, W.R., DeBenedetti, W.J., Hines, M.A., Novoselov, K.S., Abruña, H.D., Huang, F. and Frank, O., Advanced Materials Interfaces 7, no. 23 (2020): 2001324.
[3] Velicky, M., Rodriguez, A., Bousa, M., Krayev, A.V., Vondracek, M., Honolka, J., Ahmadi, M., Donnelly, G.E., Huang, F., Abruna, H.D. and Novoselov, K.S., The journal of physical chemistry letters 11, no. 15 (2020): 6112-6118.
[4] Rodriguez, A., Velický, M., Kalbáč, M., Frank, O., Řáhová, J., Zólyomi, V. and Koltai, J., Physical Review B 105, no. 19 (2022): 195413.

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Transient Electrochemical Tip Surface-Enhanced Raman Spectroscopy (EC-Tip-SERS): Concept and Applications in Electrocatalysis and Material Science

The development of electrochemical techniques combined to Raman spectroscopy such as electrochemical Tip- or Surface- Enhanced Raman spectroscopy (EC-TERS or EC-SERS) have attracted considerable attention over the past years by the scientific community. This spectro-electrochemical combination provides an accurate view over electrochemical processes occurring at an electrode by acquiring simultaneously local topography, and vibrational fingerprints about the material or molecules under potential control.[1] Based on the use of an insulated TERS tip, we introduced recently a new approach that we called EC-Tip-SERS (Figure 1). Here, electroactive molecules are adsorbed directly onto the tip that acts both as working microelectrode and single hotspot for SERS.[3] Although the spatial resolution is lost in this configuration, interesting transient mechanistic information can be obtained. In this communication, we will present first the use of this technique on a redox- and Raman- active model molecule, the Nile blue, in which a temporal resolution in the order of millisecond can be easily attained. Then, we will consider the use of Tip-SERS in probing molecular motion within rotaxane-based giant assemblies containing porphyrins derivatives. Finally, we will demonstrate the use of transient EC-Tip-SERS in scrutinizing electrocatalytic transient mechanisms, such as those associated to the oxygen reduction reaction towards hydrogen peroxide in water using viologen SAMs as electrocatalyts.

References

[1] Ding, S. Y., Yi, J., Li, J. F., Ren, B., Wu, D. Y., Panneerselvam, R., & Tian, Z. Q. Nature Reviews Materials, 1, (2016) 1-16.
[2] Touzalin, T., Joiret, S., Maisonhaute, E., & Lucas, I. T. Analytical chemistry, 89 (2017) 8974-8980.

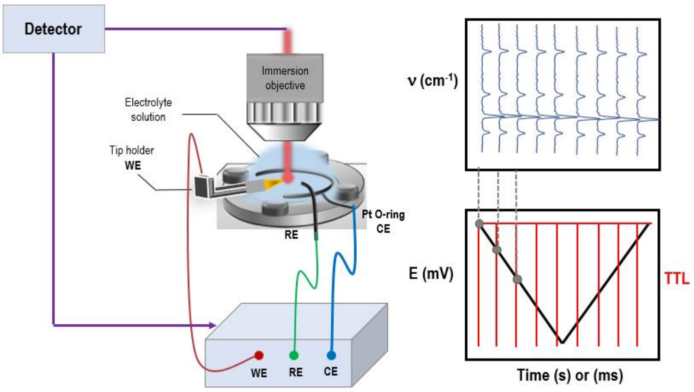

Figure 1. Transient EC-Tip-SERS setup and operando acquisitions.

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Can a low-cost nano-rough gold substrate compete with commercial SERS substrates?

Surface Enhanced Raman Spectroscopy (SERS) is a powerful non-invasive technique to detect and identify traces of molecules in a complex mixture. The accurate identification of molecules is based on the detection of distinctive vibrational modes characteristic of molecule adsorbed onto the surface. Thus, it is essential that the SERS support provides a SERS signal with the best spectral quality and sufficiently distinct from the noise signal of a control sample. We recently optimized an experimental procedure to elaborate nanorough (RMS= 2 ± 0.2 nm) gold SERS substrates. In order to verify the detection capability of our substrate for sensing applications, we compared its sensitivity to three different commercial SERS substrates: Gold nanostructured supports from Hamamatsu (Japan), Premium Ag-Au supports from SERSitive (Poland) and RAM-SERS-Au from Ocean Insight (USA). SERS substrates were dipped into solutions of thiophenol (molecule commonly used in detection test) at 10^{-6} M and 10^{-8} M. SERS measurements were performed systematically over an area of 20×20 µm² with 632.8 nm and 785 nm wavelength excitations. Depending on the topography and roughness of the substrates (Figure 1 B), x50 or x100 objectives were used. The map spectra were collected for quantitative and statistical SERS analysis. As an example, the average spectra of each map can be compared in Figure 1 A. Our results demonstrate that it is not the most sensitive (Raman intensity / Laser power ratio) SERS substrate that necessarily generates the best quality (low baseline intensity and high signal-to-noise ratio) spectra. We will show how our nanorough gold substrate can detect and identify model molecules in binary systems by using statistical tools and multivariate data analysis.

Figures

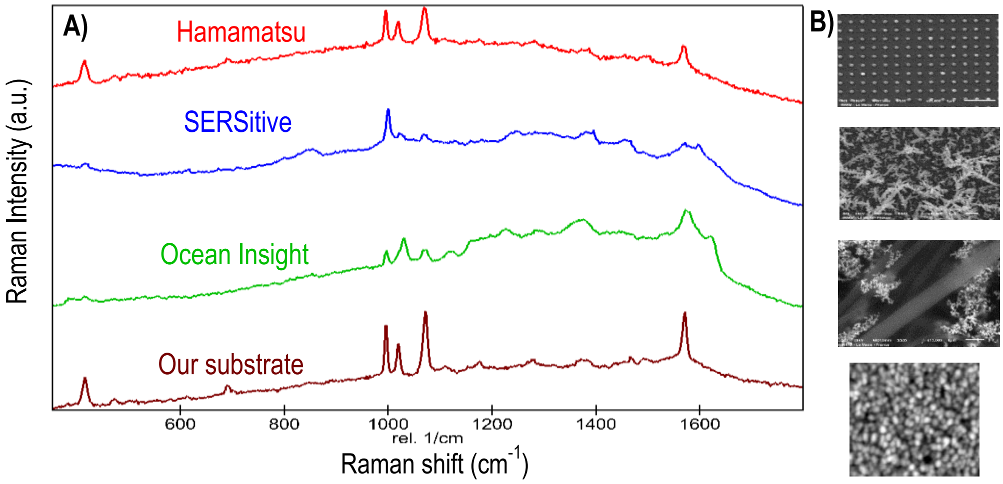

Figure 1: A) Average SERS spectra of thiophenol on Hamamatsu (red), SERSitive (blue), Ocean Insight (green) and on the nanorough gold substrate (brown) at 633 nm, after immersion in a 10^{-8} M thiophenol solution. B) SEM images of Hamamatsu, SERSitive and Ocean Insight surfaces, and AFM image of our substrate.

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Interlaboratory comparison on relative quantification of titanium dioxide (TiO_2) polymorphs in binary mixtures by Raman spectroscopy

Titanium dioxide (TiO_2) is a prominent semiconductor in industry and research that can be employed for a variety of applications. It is the most widely utilized white pigment in dyes and paints in the world, while also being of interest for its photocatalytic activity, as a component in pharmaceutical production, and as a food additive (E171). Its polymorphs of most industrial interest are anatase and rutile. These forms exhibit distinct physical and chemical properties (e.g. density, color, ultraviolet absorption, band gap) and differ in market price: from this, the industrial necessity of analytical methods for distinguishing and quantifying them arises.

ASTM D3720−90(2019) establishes the use of X-ray diffraction (XRD) as the current standard technique to quantify relative concentrations of these two TiO_2 phases; however, the method focuses on samples approaching 100 % purity of one of the two forms [1]. Moreover, this is a rather lengthy procedure, whose measurements can be affected by variability in the preparation of specimens and by specific contaminants.

Raman spectroscopy is a convenient technique for the characterization of TiO_2 and its polymorphs, because of the high cross section and distinct signals of its forms, and the minimal sample preparation required. The main limitation to the diffusion of Raman as a normatively accepted quantification technique is the lack of standardization, in terms of reference materials as well as analytical procedures and data processing; this has been exacerbated in the last few years by the widespread adoption of multivariate analysis methods in the field, often providing little information about employed procedures and parameters and with no reproducibility effort [3]. For these reasons, the Versailles Project on Advanced Materials and Standards (VAMAS) formed the Technical Working Area 42 (TWA 42) – “Raman spectroscopy and microscopy” [2].

In this prenormative study, the development and results of the interlaboratory comparison (ILC) conducted in the framework of VAMAS TWA 42 as Project 2 – “Raman spectroscopy for TiO_2 nanoparticles mixtures”, will be presented. The ILC, comprising 10 participants from 9 countries and 11 experimental setups, investigated the feasibility and metrological uncertainty of Raman microspectroscopy for relative quantification of anatase-rutile binary mixtures sourced from commercial powders (E171) throughout the whole spectrum of ratios, and established standard operating procedures for preparation of stable samples apt for international transportation, low-variance spectral acquisition by surface mapping, and multivariate data analysis by partial least squares (PLS). All models succeeded to estimate the ratios with accuracies and precisions of less than 3 % in the 5 % – 95 % range, while models constructed on most datasets suggested the possibility of surpassing this performance by a great margin. These results demonstrate the potential of Raman spectroscopy for becoming an official method for relative quantification of great industrial impact worldwide.

References

[1] ASTM International, ASTM D3720−90(2019), “Standard Test Method for Ratio of Anatase to Rutile in Titanium Dioxide Pigments by X-Ray Diffraction”.
[2] http://www.vamas.org/twa42/index.html
[3] Haibe-Kains, B., Adam, G.A., Hosny, A., Khodakarami, F., Waldron, L., Wang, B., McIntosh, C., Goldenberg, A., Kundaje, A., Greene, C.S. and Broderick, T., *Nature*, **586**.7829 (2020), E14-E16.

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Correlative Spectroscopy and Microscopy Analysis of Micro- and Nanoplastics and Their Effects on Cells and Tissues

Plastics environmental pollution evolved into a planetary problem over the last decades. Especially the micro- and nanoplastics (MNPs) particles constitute a potential health hazard for humans because of ingestion and inhalation. To assess the exposure level and impact on human health, we developed a novel analytical and automatic relocalization workflow using the Nano-Global Positioning System (nanoGPS) and Particle Finder technologies from Horiba [1]. This workflow is based on the application of Raman spectroscopy (spontaneous and stimulated) supported by complementary microscopy techniques (optical, fluorescence, electron) at the same region of interest in method-specific instruments from different manufacturers. Micro-Raman spectroscopy combined with optical microscopy was used to quantify microplastics, pigment, and additive particles contamination in bottled mineral water with the smallest analysed particle size of ~1 µm [2]. To overcome optical resolution, scanning electron microscopy (SEM) was employed to exclude both overestimation of particle size and underestimation of particle number for clustered MNPs. Moreover, single nanoplastics particles found by SEM were blindly measured by micro-Raman through relocalization and overlapping of SEM and optical images [3]. Next, the influence of MNPs as found in bottled mineral water on in-vivo human podocytes as representative kidney cells prone to accumulation of particles during lifetime was investigated. We observed clear changes in the biological features of plastics-treated cells compared to non-treated controls, attributed to cell damage through surface adhesion and uptake of plastic particles, as confirmed by cell viability fluorescence assays [1]. Feeding experiments on mice showed increased accumulation of MNPs in tissues from various organs after dextran sulfate sodium (DSS)-induced colitis. This model is similar with human ulcerative colitis characterized by damaged mucosal barrier function facilitating the transfer of MNPs from inflamed gastrointestinal tract to other organs. Thus, Raman integrated in a correlative workflow enables the chemical identification, localization, counting, and risk assessment of MNPs in water and complex biological matrices.

References

[1] G. Sarau, M. Yarbakht, B. E. Oßmann, L. Kling, J. Ast, F. Vollnhals, J. M. Deile, M. Schiffer, S. H. Christiansen, Horiba Readout, 54 (2020) 23-32
[2] B. E. Oßmann, G. Sarau, H. Holtmannspötter, M. Pischetsrieder, S. H. Christiansen, W. Dicke, Water Research, 141 (2018) 307-316
[3] G. Sarau, L. Kling, B. E. Oßmann, A. K. Unger, F. Vogler, S. H. Christiansen, Applied Spectroscopy, 74 (2020) 1155-1160

Figures

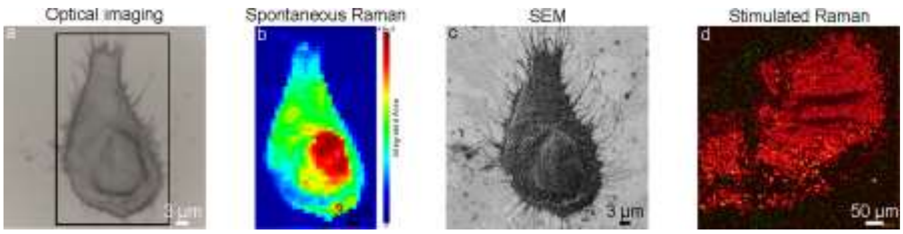

Figure 1: Spectroscopy and microscopy workflow applied to podocytes (a, b, c) and accumulation of MNPs in tissues (d).

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Visual Exploration of Raman Spectra (Open Source Python Toolkit)

We are witnesses of the proliferation of Raman spectroscopy in wide range of areas from industry to academic research. However, regardless of domain, visual exploration of experimental data is almost always an indispensable step allowing us to gain insight of the processes at work in our sample.

In parallel, modern Raman spectrometers allow us to record an evergrowing quantity of spectra in rather short time (as maps for example), and therefore require performant tools for analysis of these big datasets (~10^9 intensity values). Having such amount of data at our disposal, one naturaly turns to machine-learning algortihms to extract meaning. And arguably the most widespread modern machine learning tools use python for its front-end (scikit-learn, TensorFlow, PyTorch).

Furthermore, the growing need to ensure reproducibility of results in scientific research, incites us to provide the explicit and verifiable code for all the steps undertaken during the data analysis.

With all of the above in mind, we engaged in developing a python tool for intuitive and ergonomic exploration of hyperspectral images, irrespective of spectrometer provider. In addition, we also developped several interactive tools facilitating the choice of parameters for typical spectra processing steps (baseline correction, denoising, CR correction, etc).

The main part of this talk will consist of a live demonstration of some of the capabilities of the “SpectraPy” toolkit.

If the allocated time permits, we will briefly present a typical workflow we use for the deconvolution of Raman spectra, namely the sequential use of PCA, NMF and MCR (this will be further developed in an usecase example presented by Ekaterina BUROV).

References

[1] D. Hunter, "Matplotlib: A 2D Graphics Environment", Computing in Science & Engineering, vol. 9, no. 3, pp. 90-95, 2007..
[2] Hoyer, S. & Hamman, J., (2017). xarray: N-D labeled Arrays and Datasets in Python. Journal of Open Research Software. 5(1), p.10. DOI: https://doi.org/10.5334/jors.148
[3] Harris, C.R., Millman, K.J., van der Walt, S.J. et al. Array programming with NumPy. Nature 585, 357–362 (2020). DOI: 10.1038/s41586-020-2649-2.

Figures

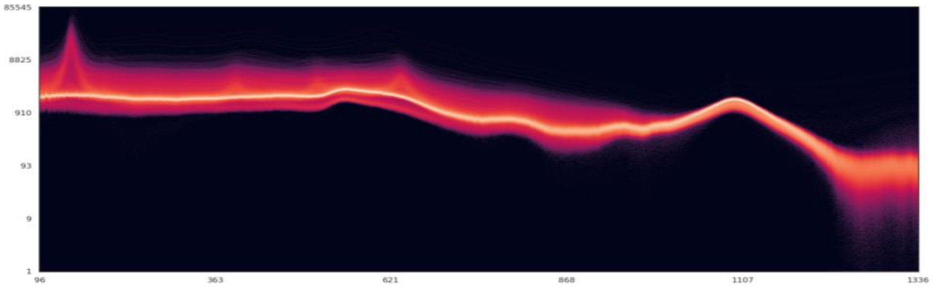

Figure 1: Histogram-like representation of ~40k spectra

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Micro-Raman spectroscopic estimation of the volume and surface temperature of GaN-based electronic devices

GaN-based electronic devices are promising components for radar and telecommunication applications [1]. Unfortunately, the reduction in size and increase in power dissipation of these devices lead to increasingly higher operating temperatures. As a result, their electrical properties and reliability can be degraded by self-heating effects. Therefore, it is crucial to accurately estimate the channel temperature in biased GaN-based components to improve their performance and their reliability by optimizing their thermal management. An example of the studied GaN-based device is shown in Figure 1-a. To estimate the self-heating temperature (ΔT) of these devices, micro-Raman spectroscopy is a good technique allowing a spatial resolution of about 1 µm. It is generally used to estimate the volume average temperature of the GaN layer. When the device is biased, its temperature increases due to the Joule effect resulting in a shift of Raman modes attributed to the GaN semiconductor that are sensitive to this temperature change. For example, Figure 1-b shows a decrease in the position of the E_2(high) mode of the GaN layer for unbiased and biased device. We can see that the temperature induces a shift in the Raman mode position. Thus, the self-heating temperature can be deduced using a temperature calibration curve, as presented in Figure 1-c for E_2(high) mode of GaN. In these conditions, the estimated ΔT is 196 °C. However, the temperature of the metal contacts cannot be directly estimated by Raman spectroscopy. To circumvent this problem, the only solution is the use of the Raman micro-thermometers, such as CeO_2 particles. By measuring the Raman band shift related to these microparticles, the ΔT of the metal contact surface can be evaluated. Since the micro-Raman thermometers are deposited on the entire device, ΔT of the GaN semiconductor surface can also be measured. In conclusion, the use of micro-Raman spectroscopy combined with CeO_2 micro-Raman thermometers is the only optical technique to simultaneously estimate the ΔT of a semiconductor surface, a metal surface and a volume average through the GaN layer of a biased GaN-based electronic device.

References

[1] G. Brocero, Y. Guhel, P. Eudeline, J. P. Sipma, C. Gaquière, B. Boudart, IEEE Trans. Electron Devices 66, n° 10 (2019) pp. 4156-4163.

Figures

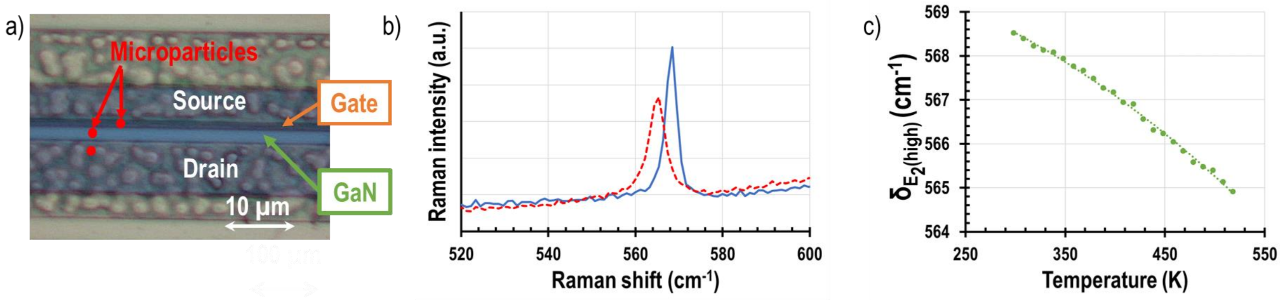

Figure 1: (a) Photograph of the studied component (b) Raman spectra of E_2(high) mode of GaN obtained for unbiased (solid line) and biased device (dashed line) and (c) temperature calibration curve of E_2(high) mode of GaN

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Strong correlations between optical near-field microscopy and far-field Raman imaging on nanorough gold SERS substrates

It is largely considered that the Surface Enhanced Raman Scattering (SERS) effect is mainly due to the presence of localized electromagnetic fields (known as hot spots) on metallic surface under irradiation. The origin and the role of hot spots on a plasmonic material have been widely studied. However, since hot spots are due to nanoscale surface singularities, it remains a challenge to control the density of singularities on a surface by depositing nanoparticles from a solution or by depositing metallic grains by vapor deposition technique for instance. Although the thermal evaporation and the sputtering techniques are not commonly used to elaborate SERS surfaces [1,2], we recently optimized procedures to elaborate efficient nanorough gold SERS substrates.

The modification of deposition parameters can induce variations of the surface topography thus leading to variations in the SERS enhancement factor. Raman mapping were recorded at λ = 633 nm on different nanorough gold substrates after immersion in a 10^{-6} M solution of thiophenol for 10 minutes. It is then possible to analyze the intensity distribution and the average Raman intensity on each substrate. By using near-field microscopy known as PhotoEmission Electron Microscopy (PEEM), it is possible to study densities of hot-spots and their energy distributions.

Here, we will show how near-field optical microscopy (PEEM) and far-field Raman scattering are strongly correlated when it comes to quantifying surface physical properties. These results allow to better understand the SERS phenomena on a plasmonic metal surface, in addition to being able to predict the relative variations of the Raman enhancement factors by the quantification of hot spots on a surface.

References

[1] A. Merlen, V. Gadenne, al. "Surface Enhanced Raman Spectroscopy of Organic Molecules Deposited on Gold Sputtered Substrates". *Nanotechnology 20* (21),**2009**, 215705.

[2] M. Edely, N. Delorme, D. Siniscalco, J.-F Bardeau."Alternative Strategy Based on Scanning Probe Lithography for Patterning Complex Metallic Nanostrutures on Rigid or Flexible Substrates". *Advanced Materials Technologies* **2018**, *3* (11), 1800134.

Figures

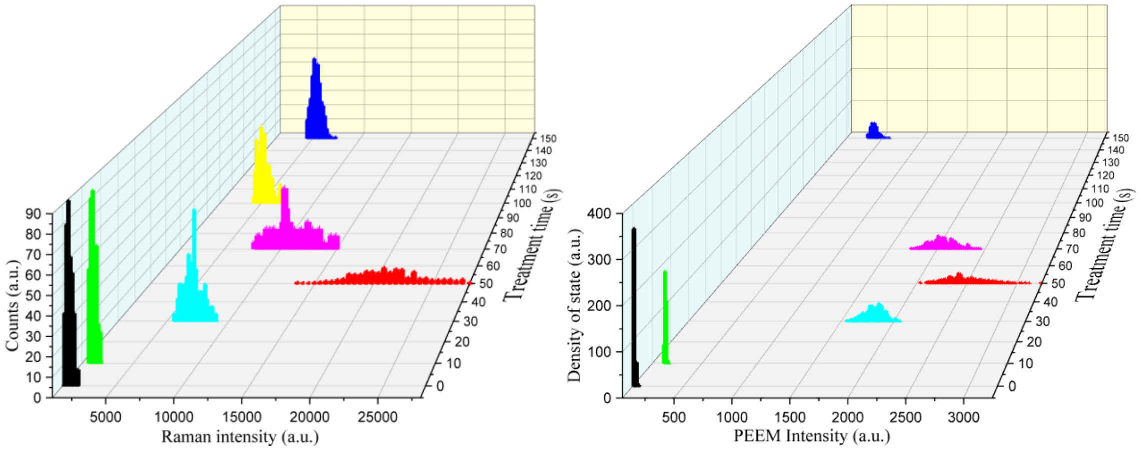

Figure 1. a) Raman intensity distributions function of treatment time b) PEEM Intensity function of treatment time

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Femtosecond Stimulated Raman Microscopy: A Novel Method for studying Liquid-Liquid Phase Separation

Liquid-liquid phase separation (LLPS) phenomena play a central role in the formation of membranelles organelles in cells [1] and in the synthesis of stiff proteinaceous biomaterials [2]. Liquid–liquid phase separation of macromolecules is referred to as coacervationion and it is proposed that complex coacervates played an important role in the origin of life [3]. In the last decade, the interest in synthetic coacervates grew for its application in complex encapsulation of, for example, proteins [4]. Two major challenges need to be met when studying phase-separation processes: (i) The quantity of material required and (ii) the need to use multiple complex measurement techniques. Raman microscopy is a powerful technique that can overcome these difficulties, but until today only a few studies used Raman techniques to investigate the coacervation phenomena.

We use femtosecond stimulated Raman microscopy (FSRM) as a novel method to investigate LLPS. FSRM is a non-linear imaging technique able to achieve full spectral coverage for each pixel with an acquisition time as fast as 0.1 ms and was already successfully applied to polymer characterization. [5,6] First FSRM results on polymeric coacervates, formed by the polyelectrolytes Poly(sodium styrene sulfonate) (PSSS) and Poly(diallyldimethylammonium chloride) (PDADMAC), will be presented.

References

[1] Shin, Y., Brangwynne, C. P., Science, 6357 (2017) 1253
[2] Heim, M., Keerl, D., Scheibel, T. Angewandte, Chemie International, 20 (2009) 3584-3596
[3] Oparin, A. I., Oliver & Boyd, Edinburgh & Londo, 3rd Ed (1953) 495 pp
[4] McTigue W. C. B., Perry, S.L., Small, 16 (2020) 1907671
[5] Ploetz, E., Laimgruber, S., Berner, S., Zinth, W., Gilch, P. Applied Physics B, 87 (3) (2007) 389-393.
[6] Czerwinski, L., Nixdorf, J., Di Florio, G., Gilch, P. Optics Letters 41 (2016) 3021-3024

Figures

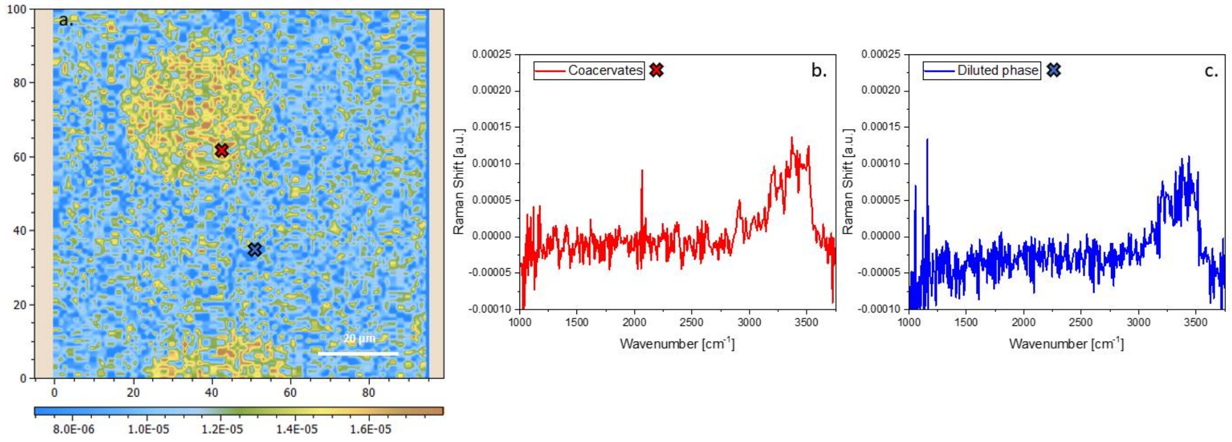

Figure 1: (a.) FSRM chemical map of a PSSS/PDADMAC coacervate in water. It has100x95 pixels with a resolution of 1 µm, and was recorded in ~ 25 min. The map is colour-coded for the intensity of the polymer C-H stretch peak. (b) Raman spectrum from the map coacervate region and (c) Raman spectrum from the map diluted phase region.

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In-situ Raman spectroelectrochemistry of graphene in concentrated aqueous electrolytes

The ionic adsorption at electrode surface changes the chemical potential which has a substantial influence to modulate the electronic properties of material[1]. The interpretation of the role of specific ion on electrolyte/material interface during electrochemical process is not a simple task due to the complex interplay between the material's properties and the electrochemical process. Therefore, a combination of *in-situ* Raman microspectroscopy with electrochemistry is an intriguing technique that can provide the valuable information about the electrochemical behavior of the layered material in an aqueous medium[2]. We performed µ-droplet in-situ Raman spectroelectrochemistry (µ-SEC) measurements on monolayer graphene in concentrated aqueous electrolytes of different ionic type and ionic strength to demonstrate the charge transfer doping (electron, hole) with alteration in the structural properties of graphene.

We observed a shift in G peak position with gating of monolayer graphene by applied potential and monitored the position of the G peak minimum corresponding to the charge neutrality point (CNP). The different electrolytes have different CNP in graphene which could correspond to minimum in charge carrier density. However, the overall shift rate of the G peak ($\Delta\omega$) of graphene with potential was observed to be similar regardless of the ionic type and ionic strength. Also, we calculated the Fermi energy shift for 2.4M $Al(ClO_4)_3$ electrolyte and calculated the doping efficiency in graphene with reference to the gate voltage. The doping efficiency was about 60 % in the hole doping regime at the maximum gate voltage of 1.6. The decrease in doping efficiency is attributed to the potential drop across the electrolyte/graphene interface.

References

[1] S. Pisana, M. Lazzeri, C. Casiraghi, K.S. Novoselov, A.K. Geim, A.C. Ferrari, F. Mauri, Nat. Mater. 6 (2007) 198–201.

[2] M. Jindra, M. Velický, M. Bouša, G. Abbas, M. Kalbáč, O. Frank, J. Phys. Chem. Lett. 13 (2022) 642–648.

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Polarized Raman Spectroscopy of boron-doped diamond

Raman spectroscopy is a fast and non-destructive method for the characterization of the composition of materials. Polarized Raman spectroscopy or angle resolved Raman measurement is now a rising analysis technique in material science. In particular, it allows the determination of the crystalline axis of the sample. Boron doped diamond is important in material science for electrochemical, electronic, and optoelectronic device applications. Using Raman spectroscopy, one can easily determine the concentration of boron in heavily doped diamond with metallic conductivity. Although the Raman spectrum the heavily boron-doped diamond (hBDD) can be fitted by a combination of classical model electronic Raman scattering and Fano effect, several features of hBDD remain unclear. In this work, we use polarized Raman spectroscopy to better understand the Raman spectrum of hBDD. Three plasma enhanced chemical vapor deposition epitaxial boron doped diamond layers with three different crystalline orientations (100, 111, and 113) have been studied using different excitation wavelengths (325, 488, 514, and 785 nm). The boron concentration within the epitaxial layers was determined from the unperturbed FWHM of the diamond zone-center phonon peak. Polarized Raman results varies with the crystalline orientation and the excitation wavelength. Collected spectra are fitted using a combination of classical model electronic Raman scattering and Fano effect. This analysis evidence the presence a new Raman peaks and a variation of the electronic Raman scattering with the crystalline orientation and the light polarization.

References

[1] V. Mortet et. al., Carbon, 2020, 168, 319.
[2] H. Zobeiri et. al., Journal of Physical Chemistry C, 2019, 123, 23236.
[3] Y. Chang et. al., Crystals, 2021, 11, 626.
[4] J. Kim et. al., J. Phys.: Condens. Matter. 2020, 32, 343001.

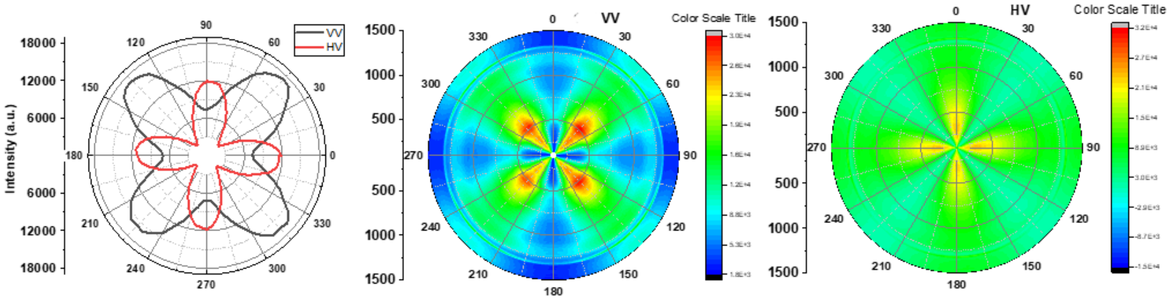

Figure 1: Raman intensity distribution of backscattering for the parallel (VV) and vertical (HV) polarization.

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Collective Vibrational Effects in Carbon Nanotube Coils

Carbon nanotubes (CNTs) are tiny hollow cylinders made of carbon. Raman spectroscopy is one of the most widespread techniques for the analysis of CNT, as it can identify their microscopic structure. In particular, much attention is paid to the low frequency region where the radial breathing mode peak is observed. For isolated tubes, a single peak is observed with a frequency that is inversely proportional to the tube's diameter. When identical CNTs are packed into bundles their vibrational properties were predicted to change and additional low-frequency modes were expected in the Raman spectrum [1]. However, the experimental study of collective vibrations has been limited due to the difficulty in obtaining homogeneous chirality bundles. Here, we present a Raman study of the collective vibrational modes arising from homogeneous bundles formed by a SWCNT coil. A defect-free coil forms a bundle with a single chirality CNT in the radial shape [2,3]. In such coils we observe two breathing-like modes (BM), in contrast to the single radial breathing mode characteristic for isolated tubes. We investigate the exciton-phonon coupling for these modes with resonant Raman spectroscopy finfing the same resonance energy for both BM peaks. Additionally, we study the diameter dependence of vibrational coupling by analyzing different coils and other bundling geometries. We compare our experimental findings with theoretical lattice dynamics of infinite bundles of identical nanotubes. These results provide an insight into intra-tube lattice dynamics in carbon nanotubes bundles for better understanding of collective vibrational effects.

References

[1] Popov, V.N. and Henrard, L., 2001. Evidence for the existence of two breathinglike phonon modes in infinite bundles of single-walled carbon nanotubes. Physical Review B, 63(23), p.233407.

[2] Shadmi, N., Kremen, A., Frenkel, Y., Lapin, Z.J., Machado, L.D., Legoas, S.B., Bitton, O., Rechav, K., Popovitz-Biro, R., Galvao, D.S. and Jorio, A., 2016, 16(4), pp.2152-2158.

[3] Nakar, D., Gordeev, G., Machado, L.D., Popovitz-Biro, R., Rechav, K., Oliveira, E.F., Kusch, P., Jorio, A., Galvao, D.S., Reich, S. and Joselevich, E., 2019. Nano Letters, 20(2), pp.953-962.

Figures

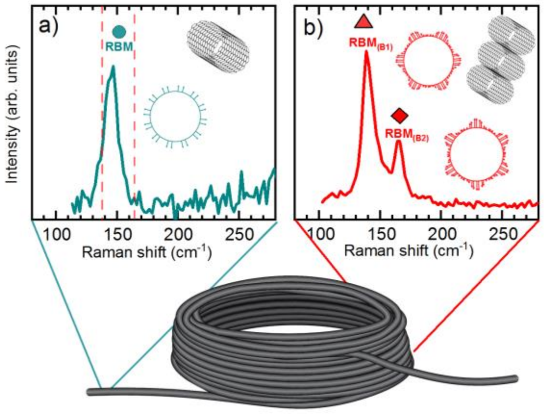

Figure 1: Raman spectroscopy of the Radial breathing modes of carbon nanotube coil. a) Raman spectra for tail and coil (isolated vs bundles effects). The peaks originating from collective vibrations are observed by RBM$_{(B1)}$ and RBM$_{(B2)}$.

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High-speed Multicolor Stimulated Raman Imaging Enabled by a Compact and Robust Light Source

We present our recent developments in utilizing a compact and portable light source for high-speed multicolor stimulated Raman scattering imaging (SRS) in biomedical and medical environments.

For visualizing cells and tissue in SRS with high chemical specificity, successive images at multiple vibrational resonances must be acquired at video-rate speed. Recent approaches to video-rate multicolor SRS, based on parallel laser amplifiers or spectral focusing techniques [1,2,3], indeed allowed wavelength switching on a timescale of (sub)milliseconds, but restricted the tuning-bandwidth to below 300 cm^{-1} at maximum, significantly limiting the chemical specificity. In contrast, the here presented all-fiber light source is tunable within milliseconds across the broad spectral range between 700 and 3300 cm^{-1}, spanning the fingerprint, silent and high-wavenumber regions. To demonstrate the capabilities of the light source, it was applied in a proof-of-principle experiment for the differentiation of lipids and deuterated components with video-rate multicolor SRS imaging [4]. Successive images of the same sample were acquired with an acquisition time of 125 ms for each image (pixel dwell time of 750 ns, 100 x 100 pixel), limited only by the scanning speed and the sampling rate of the used home-built microscope. The excitation was switched in a frame-by-frame manner between 2150 and 2850 cm^{-1} in only milliseconds, a negligible time span compared to the acquisition time. As a result, a multicolor video of the sample with a frame rate of 8 Hz, i.e., a sub-framerate of 4 Hz for each wavenumber was recorded. Differentiating lipids and deuterated components with high specificity is a key requirement of several biomedical investigations, such as drug screening or imaging of metabolic changes in organisms and has not been shown with video-rate speed before. In order to evaluate the performance of the presented system for organism study, it was recently used by Hongli Ni et al. to image C.elegans in both fingerprint and C-H region [5]. Three characteristic vibrations were imaged for a quantitative analysis of the organism’s lipid metabolism: the 1650 cm^{-1} vibration (acyl C=C bond) shows the distribution of unsaturated fatty acids; the 1670 cm^{-1} vibration (sterol C=C bond) shows cholesterol distribution; the 2845 cm^{-1} vibration in the C-H region shows the overall lipid storage. Furthermore, by implementing active monitoring and closed-loop regulators, we have achieved long-term power stability with a standard deviation of less than 0.3 % and wavelength stability better than 5 pm throughout 100 h. These developments constitute necessary steps for advancing SRS imaging in terms of reliability, ease-of-use, and specificity for applications in biomedical and medical environments.

References

[1] S. Heuke, B. Sarri, X. Audier, and H. Rigneault, Opt. Lett., 43 (2018), 3582-3585.
[2] Y. Ozeki, T. Asai, J. Shou and H. Yoshimi, IEEE Journal of Selected Topics in Quantum Electronics 25 (2019), 1-11.
[3] M. Alshaykh, C. Liao, O. Sandoval, G. Gitzinger, N. Forget, D. Leaird, J. Cheng, A. Weiner, Opt. Lett. 42 (2017), 1548–1551.
[4] T. Würthwein, K. Wallmeier, M. Brinkmann, T. Hellwig, N. M. Lüpken, N. S. Lemberger, and C. Fallnich, Biomed. Opt. Express 12 (2021), 6228-6236.
[5] H. Ni, P. Lin, Y. Zhu, M. Zhang, Y. Tan, Y. Zhan, Z. Wang, and J. Cheng, Analytical Chemistry 93 (2021), 15703-15711.

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Heat transport in h-BN

2D materials have new and intriguing properties, including their thermal properties. Like 3D materials, there is a wide variety of 2D materials with all ranges of thermal conductivity that can be simply assembled on top of each other[1]. Moreover, the thermal conductivity is extremely anisotropic in these materials. It has been demonstrated in the same 2D heterostructures ratios of 3 orders of magnitude between vertical and in-plane thermal conductivity, a record. Moreover, the interest from a fundamental point of view is the appearance at room temperature of a particular regime of phonon scattering, which allows to describe the heat transport as a hydrodynamic flow [2]. Thanks to these characteristics, it is interesting to study their thermal properties.
Here, we focus on the thermal conductivity of suspended h-BN. It is an interesting material because it has a very high thermal conductivity but is electrically insulating. Nevertheless, it is difficult to heat it with a laser because of its low absorbance. To overcome this problem and to perform thermal mapping, we have made two heating bridges of Silicon between which a flake of hBN is suspended. One of the bridges is heated by Joule effect while the other one allows us to calibrate the heat flow through the 2D materials. Raman spectroscopy measurements allow to measure the temperature at each point of the system. We were able to extract a thermal conductivity of h-BN around 200°C equal to 420 W.m^{-1}.K^{-1}.

[1] Qian X et al. , Nat. Mater., 20 (2021), 1188-1202
[2] Shi L et al, Science, 364(2019), 332-333

Figures

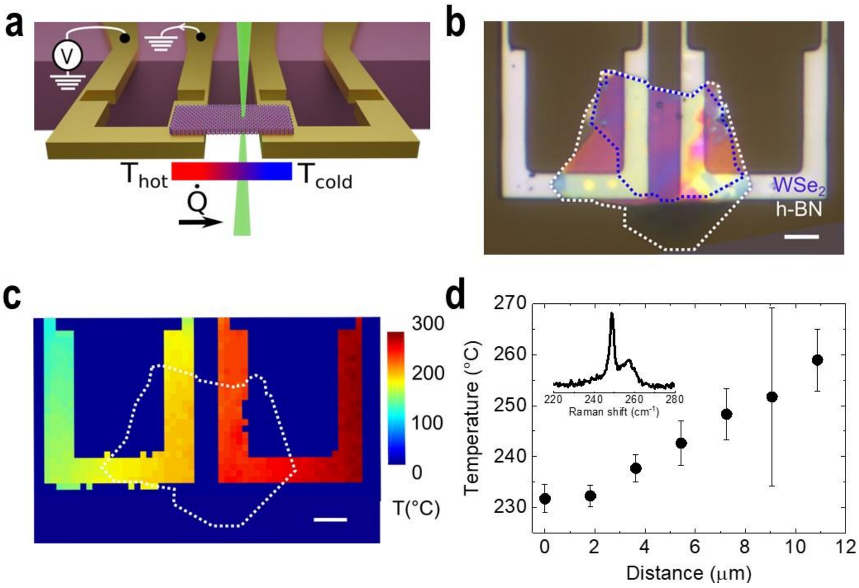

Figure 1: a) b) Schematic sketch (a) and optical image (b) of the device structure with a suspended hBN between two silicon heaters. c) Temperature map of Silicium, measured with a green laser, when one electrode is hot. d) Temperature gradiant of the 2D material between the two bridges (inset : Raman spectrum of WSe$_2$) All scales bar : 10 microns

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Defects in polymer multilayer films: A new way to investigate based on Raman microscopy

Polymer multilayer films are presents everywhere in our world. Thus, we can find them in food packaging, on car coatings, in phone protection films, among many other applications. But their characteristics are questioning as soon as a defect is present. Unfortunately, it's not easy to locate this defect, and consequently chemically characterize and identify it.

Confocal Raman microscopy is a perfect candidate for such issue, combining the high spatial resolution of optical microscopy with the chemical identification through the spectral characterization.

This combination makes our Raman confocal microscope the ideal solution for non-destructive highly resolved characterization of the defect realizing a very fast survey mapping of the sample.

Figures

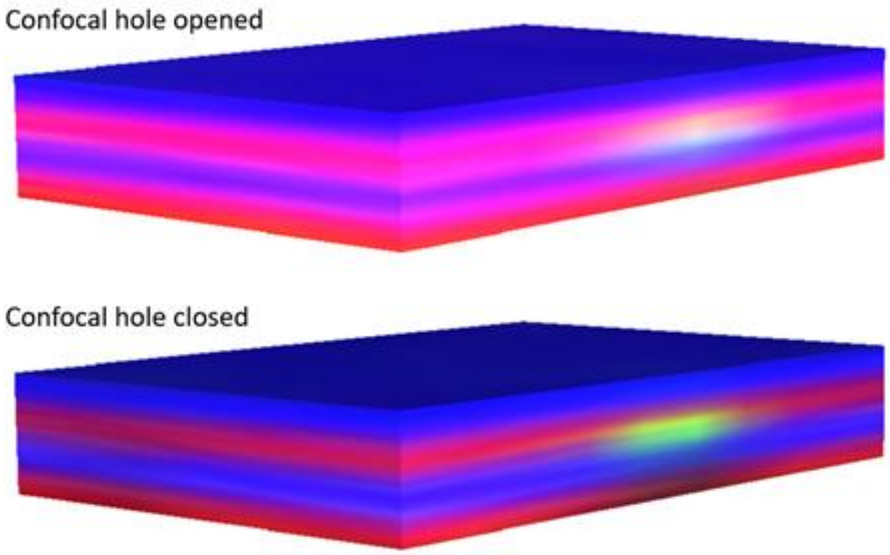

Figure 1: 3D Raman map of an feature in a multilayer polymer sample. The colors represents the different chemical fingerprint. Blue: Plastic tape. Red: Glue. Green: Feature. Map dimension: 500x500x100µm with 50x50x1µm steps. (Top) Map with confocal hole opened. (Bottom) Map with confocal hole closed.

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Life Science in Live by Nonlinear Microscope and Endoscope

Nonlinear imaging techniques, such as 2-photon/3-photon autofluorescence, second/third harmonic generation (SHG/THG), coherent anti-Stokes Raman (CARS) scattering and stimulated Raman scattering (SRS), stand out for life science applications by their label-free property. These techniques can be used to observe morphology of biological systems or targeting specific molecules in the system. Together with a fast-scanning system, nonlinear techniques can be also used to follow real-time dynamic biological process, such as animal metabolic process, molecular delivery in skin and neural activities in brain.

We developed a fast, sensitive and compact nonlinear microscope system, which includes 2-photon fluorescence, SHG and SRS imaging. Our microscope has been used for medical applications (tumor diagnose [1], organoid observation), chemical and pharmaceutical applications (cosmetic spreading, pharmaceutical tablet quality control [2]) and biological applications (metabolic process [3], molecular penetration in skin[4]).

To go one step further, we also integrate nonlinear techniques (2-photon/3-photon, SHG/THG, CARS) in a flexible endoscope (see Figure 1) [5], to access samples that cannot be placed in a microscope, and to observe biological process in a living model such as mice [6].

In conclusion, our nonlinear microscope and endoscope can provide label-free live imaging for various biological and biomedical applications and can be adapted for different samples *in vitro* and *in vivo*.

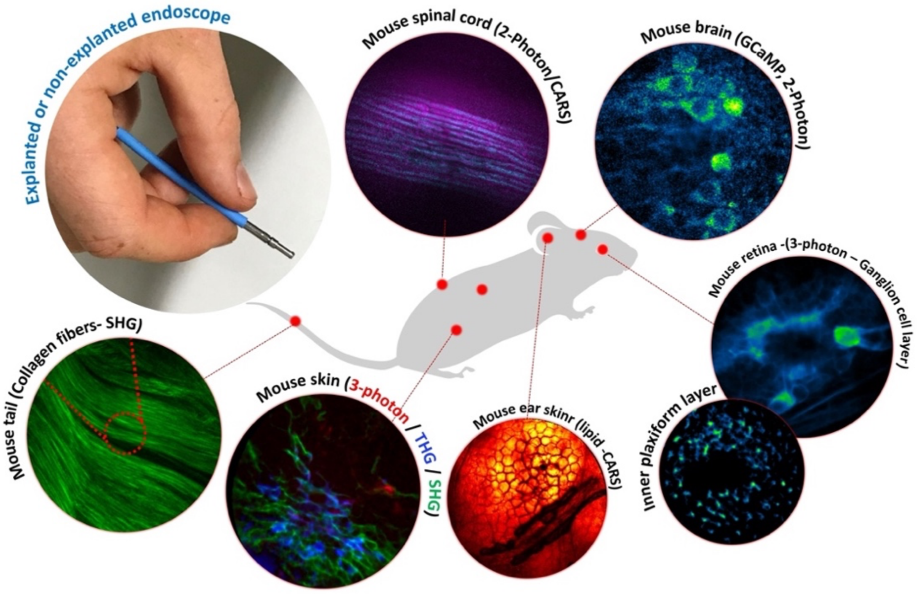

Figure 1: Imaging different locations on/in mice using nonlinear endoscope M-FIP.

References

[1] B. Sarri, et al., Biomed. Opt. Express, 10(2019) 5378-5384
[2] B. Sarri, et al., Journal of Raman Spectroscopy, 50 (2019) 1896-1904
[3] S. Heuke, et al., Biomed. Opt. Express, 12 (2021) 7780-7789
[4] X. Chen, et al., J. of Controlled Release, 200 (2015) 78-86
[5] A. Lombardini, et al.,Light : Science & Applications 7(2018) 10
[6] D. Septier, et al., Optics Express, 30(2022) 25020-25033

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Straintronics in 2D semiconductors

Two-dimensional transition metal dichalcogenides (TMDs) have been investigated for applications in optomechanics and optoelectronics thanks to their properties (thickness, high Young modulus, very low mass and direct bandgap in monolayers). The control over strain is at the heart of many new applications in these fields. To highlight the interest of this topic, we achieve strong strain tuning in suspended 2D materials via thermal expansion and tip indentation.

First, we propose a new scheme to tune efficiently the mechanical vibration of 2D suspended membrane. We investigated the efficiency of electrothermal tuning of the vibration of MoS_2 nanoresonator using Joule heating and thermal dilatation to slightly change the intrinsic strain and modify the resonant frequency using the nano-opto-elctro-mechanical platform (NOEM) shown in Figure 1. Considering these properties, we extract the thermal conductivity and demonstrate a good temperature sensitive device with a resolution of about 20mK.

Second, to reach higher strain regime, we apply a local force on the membrane with an AFM tip indentation which strongly tune the optical bandgap. The non-uniform strain, obtained in this system, leads to the diffusion of the excitons[2] and the conversion of excitons to trions[3]. We investigated locally the properties of a suspended membrane of $WS_{1.3}Se_{0.7}$ under non-uniform strain exploiting the tip enhanced photoluminescence (TEPL) under the AFM tip shown in Figure 2.

References

[1] Jaesung Lee et al., ACS Nano 2013 7 (7), 6086-6091
[2] Hyowon Moon et al., Nano Letters 2020 20 (9), 6791-6797
[3] Harats, M.G., Kirchhof, J.N., Qiao, M. et al. Nat. Photonics 14, 324–329 (2020).

Figures

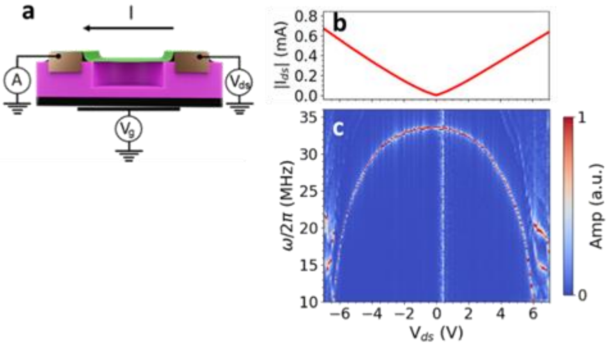

Figure 1 : a) Electrothermal setup. b) Current tension characteristics of the device. c) Very efficient electrothermal frequency tuning of the nanodrum due to the strain variations.

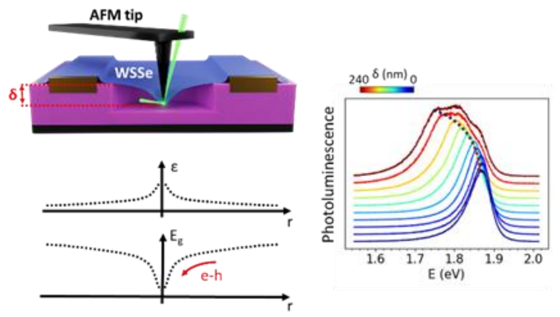

Figure 2 : a) Tip indentation setup. b) The tip indentation induces non uniform strain on the 2D semiconductor changing the gap locally. c) Variation of photoluminescence with respect to height variations of the center of the membrane.

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Correlative imaging of single graphene oxide flake including Raman microscopy technique: sample selection and limitations

Graphene is of major interest for a large number of applications currently under development. However, its production remains complex in large quantities. Graphene oxide (GO) is much easier to synthesize and is therefore often used as a precursor for the preparation of reduced graphene oxide (rGO), whose morphology and physicochemical properties tend more towards graphene as the reduction is more advanced. However, rGO contains a number of structural defects that influence its physicochemical properties, such as its electrical and thermal conductivity, etc.

To control this reduction, it is interesting to follow the evolution of these physico-chemical properties during the GO reduction process, starting with a good characterization of the properties of the initial GO. Based on its expertise in hybrid metrology specifically developed for measuring single nano-object [1], LNE has chosen to characterize the GO through the correlation of various microscopy technique on single GO flake: Raman spectroscopy/microscopy, Scanning Electron Microscopy (SEM), Atomic Force Microscopy and derivate techniques (AFM, SThM, SMM, KPFM). This correlative imaging approach implies that each limitation of each technique have to be considered to select the ideal sample and substrate. Moreover, strategy must be put in place so that when correlative microscopy is performed the location of the flakes is easy and the least invasive techniques are used before the most invasive ones. One of the limitations of Raman spectroscopy/ microscopy when performing correlative microscopy is the degradation of the sample, even at low power [2].

We show in the poster the limitation induced by the various techniques of microscopy employed, more particularly the Raman spectroscopy/microscopy.

References

[1] Crouzier, L., et al. 2019. "Development of a New Hybrid Approach Combining AFM and SEM for the Nanoparticle Dimensional Metrology." Beilstein Journal of Nanotechnology 10.
[2] Torrisi, A., et al. 2022. "Graphene oxide modifications induced by excimer laser irradiations. Surface and Interface Analysis", 54(5), 567–575.

Figures

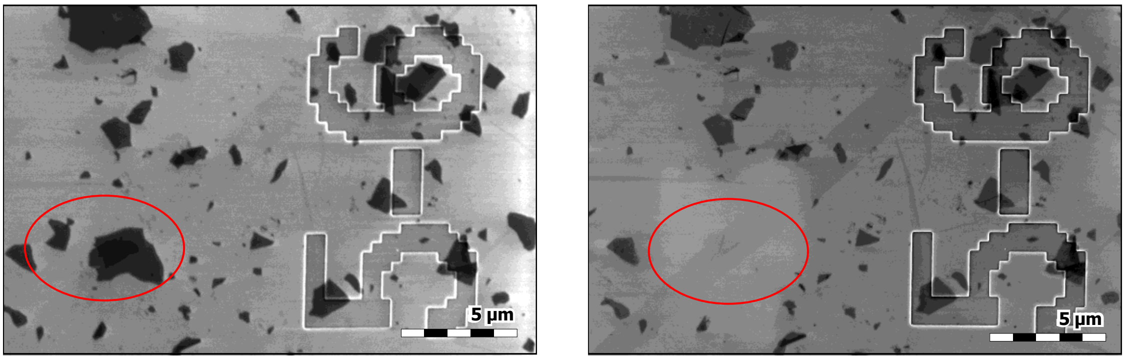

Figure 1: SEM observation of a GO flake deposited on SiO_2 substrate before (left) and after (right) Raman spectroscopy laser irradiation.

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Method for layer-resolved Raman mapping of transferred graphene

The technique for layer-resolved Raman mapping is an extension of the previously introduced method of determining the number of graphene layers [1]. It's based on the substrate's Raman-active modes intensity attenuation, caused by graphene absorption. Combining this method with the standard Raman analysis [1,2] allows the standardization of the material regardless of the number of graphene layers. This method is presented in the example of transferred graphene, decomposed into the areas of single and multiple graphene layers and characterized separately by standard Raman analysis.

References

[1] A. Dobrowolski, J. Jagiello, D. Czolak, T. Ciuk, Physica E: Low-dimensional Systems and Nanostructures, 134 (2021), 114853
[2] K. Pietak, J, Jagiello, A. Dobrowolski, R. Budzich, A. Wysmołek, T. Ciuk, Applied Physics Letters, 120 (2022), 063105

Figures

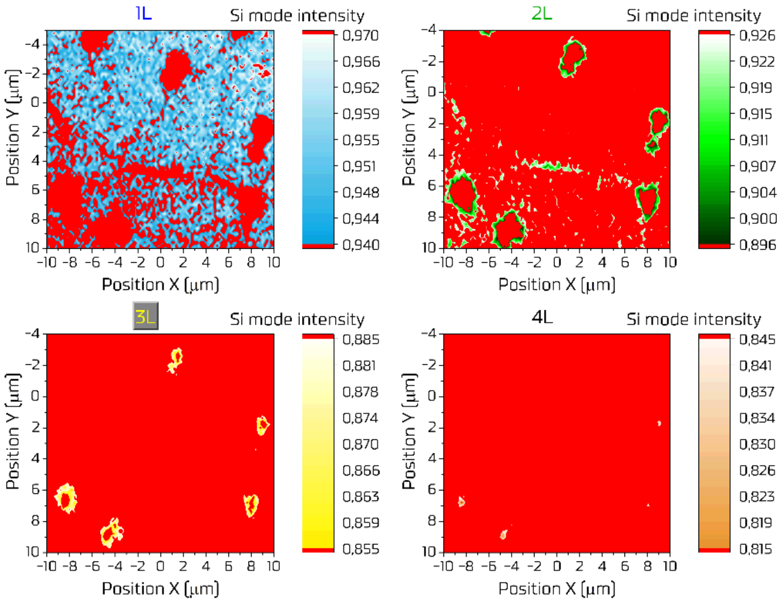

Figure 1: Layer-resolved Raman mapping of transferred graphene

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Electrochemical TERS for the *in situ* characterization of structured molecular patterns
-Towards the *operando* analysis of functional devices-

The nanostrucuration of surfaces, with thin molecular layers or specifically designed patterns, is nowadays exploited for a myriad of applications (from molecular sensing to catalysis, energy storage or conversion). Therefore, it is essential to improve both the sensitivity of the analytical methods that are used to characterize these novel materials, and the accuracy of the tools employed for the nanostructuration.
A promising candidate that fulfils these requirements is the EC-TERS (electrochemical tip-enhanced Raman spectroscopy) technique, which conjugates the high-quality results of the TERS analyses with the possibility of performing electrochemical sequences *in situ* [1,2]. More specifically, the work herein presented shows the performances of an improved EC-TERS setup, mounted in a scanning tunneling microscope (STM) [3,4], which was used to solve a complex electrochemical reaction (occurring on electroactive surface-grafted molecular layers) and gave preliminary results of surface patterning (by organic layers modification or metal oxides deposition).

References

[1] Z.-C. Zeng, S.-C. Huang, D.-Y. Wu, L.-Y. Meng, M.-H. Li, T.-X. Huang, J.-H. Zhong, X. Wang, Z.-L. Yang, B. Ren, Journal of the American Chemical Society, 137 (2015) 11928–11931
[2] G. Kang, M. Yang, M. S. Mattei, G. C. Schatz, R. P. Van Duyne, Nano Letters, 19 (2019) 2106–2113
[3] T. Touzalin, S. Joiret, I. T. Lucas, E. Maisonhaute, Electrochemical Communication, 108 (2019) 106557
[4] Fiocco A., PhD thesis' manuscript (2022)

Figure

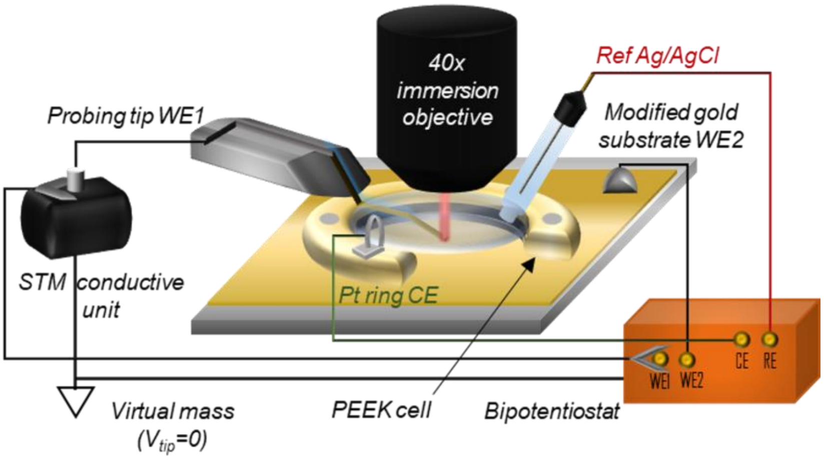

Figure 1: Schematic view of the implemented EC-STM-TERS setup

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Raman spectroscopy for measuring thermal properties of thin films and 2D materials

Measuring the thermal properties of thin films and 2D materials is an essential step in correctly assessing the suitability of new materials for many applications. For example, thermal conductivity (κ) and interfacial thermal conductance (g) are crucial in designing optimal heat management in electronic devices.

This short communication presents two Raman-based methods for measuring κ and g in thin films and 2D materials. The first, the opto-thermal Raman method, uses laser light as a heat source and Raman scattered light as a thermometer [1][2]. The second, utilize a transparent electrical heater for a heat source and unique material selectivity of Raman scattered light to directly measure temperature difference in stacked materials.

References

[1] Gertych, A. P., Czerniak-Łosiewicz, K., Łapińska, A., Świniarski, M., Ojrzyńska, M., Judek, J., & Zdrojek, M. (2021). Phonon and Thermal Properties of Thin Films Made from WS_2 Mono-and Few-Layer Flakes. The Journal of Physical Chemistry C, 125(26), 14446-14452

[2] Gertych, A. P., Łapińska, A., Czerniak-Łosiewicz, K., Dużyńska, A., Zdrojek, M., & Judek, J. (2019). Thermal properties of thin films made from MoS_2 nanoflakes and probed via statistical optothermal Raman method. Scientific reports, 9(1), 1-7.

Figures

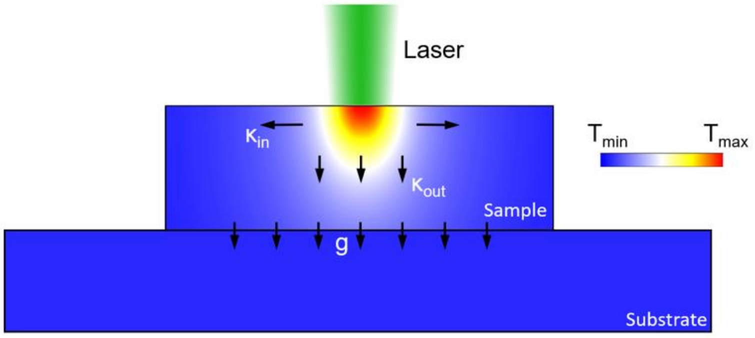

Figure 1: Schematic view of the sample heated by Raman laser.

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Characterization of cancer-associated adipocytes by Raman spectroscopy

Adipocytes are the major cellular components comprising the breast cancer microenvironment. In the early stage of breast cancer, cancer cells locally infiltrate the nearby adipose tissue, which results in the activation of adjacent adipocytes into cancer-associated adipocytes[1] (CAAs). Consequently, it gives advantages to breast cancer cells in terms of survival, growth, and metastasis. Compared to normal adipocytes, CAAs are mainly characterized by a decrease in size, lipid content, adipocyte differentiation markers, and an increase in adipokines and inflammatory factors. We propose to use Raman spectroscopy to identify new biomarkers representative of the status of CAAs.

To capture transition between adipocyte and CAAs, a 2D in vitro co-culture model, providing a contact area between adipocytes (differentiated 3T3-L1 cells) and breast cancer cells (MDA-MB-231, Claudin-low subtype) was developed. However, cell heterogeneity is a major drawback of this cell culture model. For example, each kinetic time is marked by the coexistence of immature (fibroblast-like) and mature (adipocyte-like) 3T3-L1 cells non-equally differentiated. On the other hand, the adipocyte/CAAs transition induced by breast tumor cells varies from one adipocyte to another. To address this issue, we adapted algorithmic tools, recently implemented for single cell transcriptomic analysis, to vibrational Raman spectral data. These tools, known as trajectory inference (TI) or pseudotemporal ordering[2], aim to reconstruct evolving pathways from different cell states, coexisting simultaneously in a cell population. Our research focused on the use of Partition-based graph abstraction[3] (PAGA) algorithm combined to uniform manifold approximation and projection (UMAP) to decipher adipocyte cells heterogeneity and highlight CAAs population.

We show how Raman spectroscopy can be used in association with TI approach to visualize and resolve the cell heterogeneity of this cell model. More specifically, the results support the evidence of diverse differentiated adipocyte subtypes and CAAs subpopulation. This new approach will pave the way for a better comprehension of cell heterogeneity and may reveal new molecular states and subpopulation-specific responses to external perturbations.

References

[1] Wu, Q., Li, B., Li, Z. *et al.* Cancer-associated adipocytes: key players in breast cancer progression. *J Hematol Oncol* **12**, 95 (2019).
[2] Luecken, M. D. & Theis, F. J. Current best practices in single-cell RNA-seq analysis: a tutorial. Mol. Syst. Biol. 15, e8746 (2019).
[3] Wolf, F.A. et al. PAGA: graph abstraction reconciles clustering with trajectory inference through a topology preserving map of single cells. Genome Biol 20, 59 (2019).

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Guest-Host Raman under Liquid Nitrogen Spectroscopy for the Acquisition of Improved Vibrational Spectra of Solids

Guest-host Raman under liquid nitrogen spectroscopy (GHRUNS) involves the isolation of solid-state guest molecules inside cage-like host environments for the facile acquisition of their Raman spectra. This convenient method features reduced fluorescence, the analysis of populations in their ground states, and increased signal to noise ratios. Samples are also preserved through the reduction of thermal degradation and oxidation. To demonstrate the benefits of this new method, Raman spectra of the ubiquitous molecule C_{60} inside a cage of water ice are presented. Using this technique, a new normal mode of C_{60} is elucidated. The GHRUNS methodology is of interest to those seeking to acquire and characterize the vibrational spectra, structure, and properties of emissive, air-sensitive molecules.

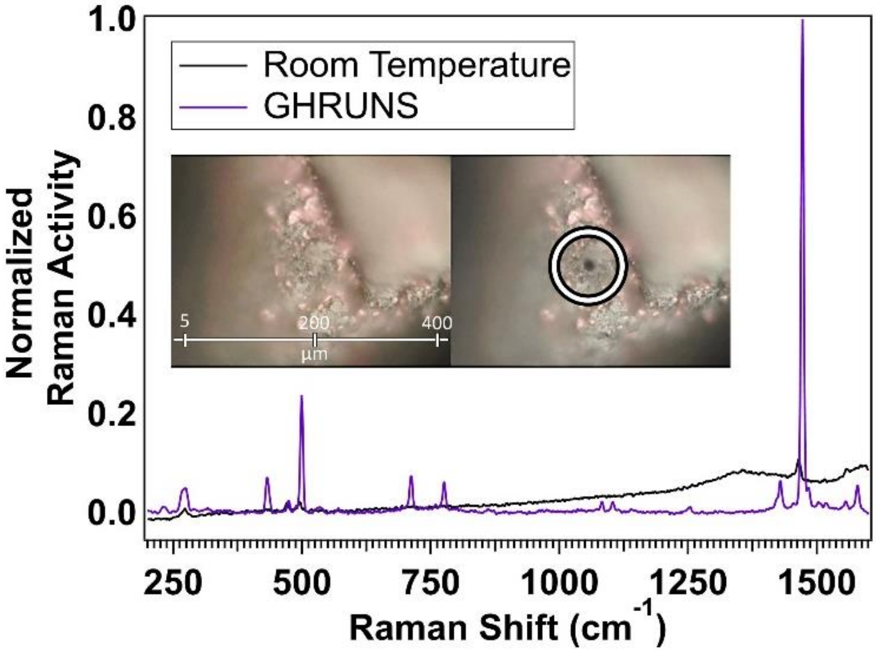

Figure 1: Raman spectrum of C_{60} at room temperature (black) and GHRUNS methodology (purple) under the same laser irradiation. The inset photograph demonstrates resulting laser damage at room temperature.

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Quantitative Raman analysis of TiO_2 thin films prepared by a sol-gel process

Titanium dioxide (TiO_2) is a material well known for its usage in photocatalysis. The two most used phases of TiO_2 are anatase and rutile. Nanocrystalline anatase is reported to be more suitable compared with nanocrystalline rutile for photocatalytic applications due to its higher surface area, enhanced charge separation efficiency and relatively larger bandgap leading to a slightly higher redox capability [1]. At atmospheric pressure, a phase transformation from anatase to rutile occurs at around 550 °C [2] and at approximately 800 °C anatase is expected to be fully converted into rutile [3]. Temperature control between these two values was proven to be a straightforward and efficient procedure to tune the relative concentration of both phases and thus to achieve a desired mixture for efficient photocatalytic activity. A quantitative determination of the phase composition of such mixtures is therefore desirable and of relevance if we wish to optimize the TiO_2 thin film photocatalytic properties. Here, we present a systematic case study regarding the quantitative Raman analysis that could be useful for the TiO_2 photocatalysis community. Our titanium dioxide thin films are synthesized using a sol-gel process and spin coated on p-type Si (100) substrates with a native oxide layer. The as-deposited TiO_2 thin films are then annealed at different temperatures from 400 °C to 800 °C for 3 hours in ambient conditions. UV-Raman (excitation wavelength of 325 nm) and visible Raman (excitation wavelength of 532 nm) spectra are taken in backscattering geometry under a microscope. Quantitative analysis is performed considering the area under the Raman peaks and the peak widths of the Raman fingerprint features of the TiO_2 anatase and rutile polymorphs [4,5]. The procedure is further complemented by and benchmarked against X-ray diffractometry results obtained on the same set of samples. The results reveal the successful Raman quantitative analysis of the TiO_2 thin film samples with the fine-tuning of their phase composition.

References

[1] Guo Q, Zhou C, Ma Z, Yang X. Fundamentals of TiO2 Photocatalysis: Concepts, Mechanisms, and Challenges. Advanced Materials 2019;31. https://doi.org/10.1002/adma.
[2] Hanaor DAH, Sorrell CC. Review of the anatase to rutile phase transformation. Journal of Materials Science 2011; 46:855–74. https://doi.org/10.1007/s10853-010-5113-0.
[3] Mei Z-G, Wang Y, Shang S, Liu Z-K. First-principles study of the mechanical properties and phase stability of TiO2. Computational Materials Science 2014; 83:114–9. https://doi.org/10.1016/j.commatsci.2013.11.020.
[4] Castrejón-Sánchez VH, Camps E, Camacho-López M. Quantification of phase content in TiO2 thin films by Raman spectroscopy. Superficies y Vacío 2014; 27:88–92.
[5] Cao G, Yi N. Quantitative Analysis of Anatase-Rutile Mixtures by Raman Spectroscopy. ChemistrySelect 2020; 5:11530–3. https://doi.org/10.1002/slct.202002931

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Enhancement of graphene-related and substrate-related Raman mode through dielectric layer deposition

Enhancement of the Raman signal intensity is currently among the most researched directions in developing Raman-based characterization techniques of all 2D materials as it elevates detection limits of their fine structural properties. The interest in Raman signal intensification is also triggered by the wide range of applications it can benefit, such as biochemistry and biosensing, polymer and materials science, catalysis, electrochemistry, the study of high-temperature processes, and the detection of hazardous gases [1]. In this work, we demonstrate a method for the enhancement of Raman active modes of hydrogen-intercalated [2] quasi-free-standing epitaxial chemical vapor deposition graphene and the underlying semi-insulating 6H–SiC(0001) substrate through constructive signal interference within atomic-layer-deposited amorphous Al_2O_3 passivation. We find that an optimum Al_2O_3 thickness of 85 nm for the graphene 2D mode and one of 82 nm for the SiC longitudinal optical A_1 mode at 964 cm^{-1} enable a 60% increase in their spectra intensities. We demonstrate the method's efficiency in Raman-based determination of the dielectric thickness and high-resolution topographic imaging of a graphene surface [1,3].

The research leading to these results has received funding from the Research Foundation Flanders (FWO) under Grant No. EOS 30467715, the National Science Centre under Grant Agreement No. OPUS 2019/33/B/ST3/02677 for project "Influence of the silicon carbide and the dielectric passivation defect structure on high-temperature electrical properties of epitaxial graphene," and the National Centre for Research and Development under Grant Agreement No. LIDER 0168/L-8/2016 for the project "Graphene on silicon carbide devices for magnetic field detection in extreme temperature conditions."

References

[1] K. Pietak, J. Jagiello, A. Dobrowolski, R. Budzich, A. Wysmolek, T. Ciuk, Applied Physics Letters, 120 (2022), 063105.
[2] M. Szary, S. El-Ahmar T. Ciuk, Applied Surface Science, 541 (2020), 158668.
[3] A. Dobrowolski, J. Jagiełło, D. Czolak, T. Ciuk, Physica E: Low-dimensional Systems and Nanostructures, 134 (2021), 114853.

Figures

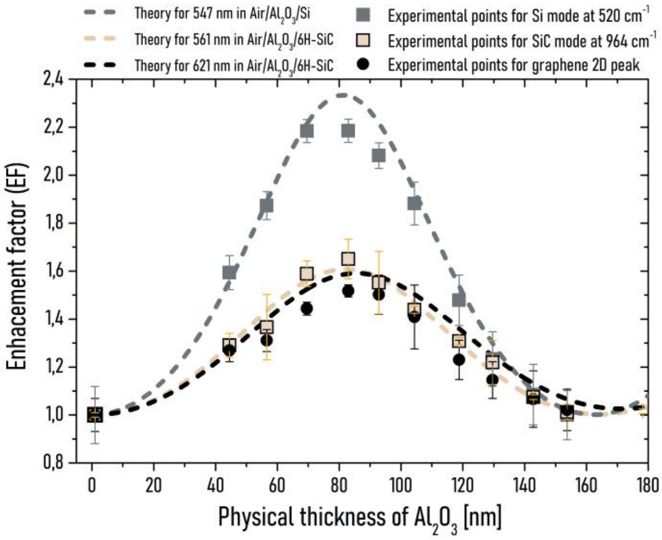

Figure 1: Theoretical (dashed lines) and experimental (square symbols) enhancement factor (EF) for the SiC LO A_1 mode at 964 cm^{-1} (marked in beige), the Si mode at 520 cm^{-1} (marked in gray), and the QFS graphene 2D mode at 2708 cm^{-1} (marked in black), all as a function of the Al_2O_3 physical thickness.

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Enhanced Tri-modal Optical-Photothermal Infrared (O-PTIR) Spectroscopy – Advances in Spatial Resolution, Sensitivity & Tri-modality (IR, Raman & Fluorescence)

Optical Photothermal Infrared (O-PTIR) spectroscopy has established itself as a cutting edge vibrational microspectroscopy tool, offering significant advantages over the traditional FTIR/QCL & Raman spectroscopic tools, providing submicron simultaneous IR+Raman microscopy, in non-contact mode with high sensitivity. The ability to collect, for the first-time submicron IR spectroscopic data in an optical microscope has enabled new research outcomes across a range of application fields, such as life sciences (cells, tissues, bacteria), polymers, cultural heritage and microplastics.

A new modality, “counter-propagating” has been engineered to provide for enhanced IR (and Raman) spatial resolution and sensitivity, through decoupling the need for a reflective objective. The IR pump beam can now be directed to the sample via the underside, thus allowing the collection objective for the visible probe (and Raman excitation beam) to be a high-NA refractive objective. This improves spatial resolution to ~300nm for both IR and Raman, whilst improving sensitivity, image quality and facilitating immersion objective studies.

To further integrate vibrational spectroscopic tools into life science workflows, we coupled widefield epifluorescence to facilitate a novel concept – fluorescence guided (or fluorescence co-located) O-PTIR microspectroscopy. Rather than, or in addition to the visible image, the fluorescence image can now be used to guide the user to the region of interest, thus combining the well-established specificity of fluorescence imaging with the broad macromolecular profiling capabilities of IR spectroscopy

Several life sciences examples from bacteria, cells and tissues will be provided to demonstrate these new capabilities and how they can enable new experiments and research findings..

Figures

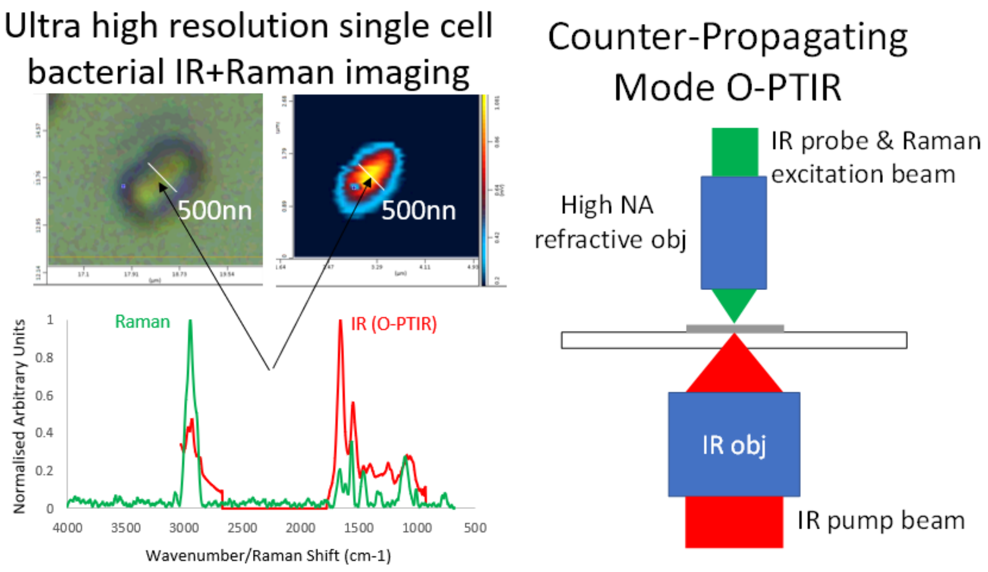

Figure 1: Left: Single E.Coli cell imaged in counter-propagating mode with 50nm pixel/step size and submicron simultaneous IR+Raman spectra from centre of bacterial cell. Right: Schematic of counter-propagating layout.

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SmartSampling™: A revolution in Raman imaging

From its beginning more than 50 years ago, the Raman microscopy went through many stages that have marked its history. Thus, starting from the point spectral acquisition at the micron scale, the capability to acquire Raman images opened the door to more and more applications. Then, the ability to the multichannel detectors to be faster and faster improved the speed of measurement and so increased the performances of such Raman imaging systems with less than a millisecond acquisition time per spectrum. However, such performances are possible only on high Raman scattering samples, reducing the concerned applications.

With our solution, we now offer the ability to all applications to improve their speed of Raman imaging. Based on the video contrast, this patented algorithm segments the map area in regions of interests of different sizes. Consequently, a quick preview based on high quality spectra is obtained in few seconds and then this rough image is improved step by step, detail by detail. Thus, good quality images are obtained after only few minutes when it needs hours or days to be completed in classical point-by-point mapping.

In this presentation, we detail how this approach will revolutionize the Raman imaging in all application domains, from physical to life sciences.

Figures

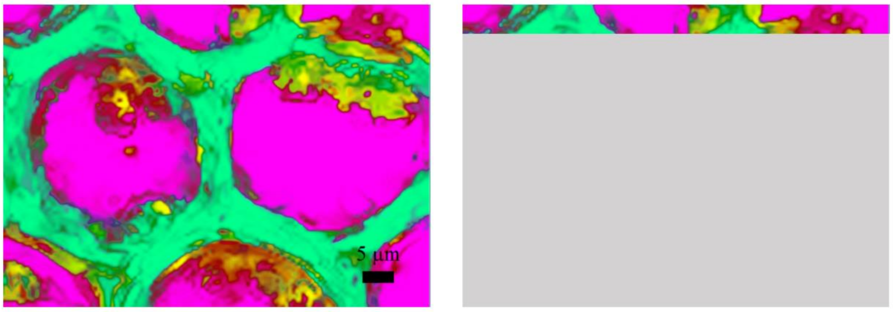

Figure 1: Covallaria cells. (Left) 14 minutes SmartSampling™ Raman image. (Right) Equivalent point by point image obtained in 14 minutes.

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Improving Nano-Biology Interaction Studies with Multi-Modal Raman & Enhanced Darkfield Optical Hyperspectral Microscopy

Effective studies at the nano-bio interface require that researchers can easily observe and measure how nanoparticles interact with a targeted in-vitro cell or ex-vivo tissue environment. HORIBA Scientific and CytoViva, Inc. now provide a new multi-modal Raman and enhanced darkfield hyperspectral microscopy system that is highly effective for nano-biology related research. This system includes patented enhanced darkfield optics that enable label-free observation of nanoparticles as small as 10nm when isolated in solution and in cells and tissue. The optical hyperspectral imaging capability enables rapid capture of large-area hyperspectral images for spectral characterization and spectral mapping of nanoparticles or their drug load. Pixel-level optical hyperspectral data is captured based on the nanoparticle's surface plasmon resonance, fluorescence emission or Rayleigh scatter. Additionally, Raman measurements from the identical field of view can be captured, which provides quantitative molecular fingerprint confirmation of the nanoparticles or other sample elements. Finally, Raman mapping of unique sample elements can also be performed when required. This presentation will provide a detailed overview of this new multi-modal imaging and spectral measurement capability. Specific illustrations of plasmonic, metal oxide, polymer and lipid-based nanoparticles interacting with cells and tissue will be presented.

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When Raman and friends go to the mountains – correlative analysis with MountainsSpectral®

Based on science's most trusted analysis software platform, MountainsSpectral® is a comprehensive, dedicated solution for processing & combining images and other data from spectroscopic techniques including Raman, TERS, IR, nanoIR, fluorescence, photoluminescence, cathodoluminescence, EDX/EDS and XPS as well as microscopy data.

In particular, it opens up new possibilities and workflows for the analysis of spectroscopic data including: spectral map processing and enhancement, colocalization for correlative analysis, topographic analysis tools for AFM images, SEM image 3D reconstruction, particle analysis and spectral analysis.

Figures

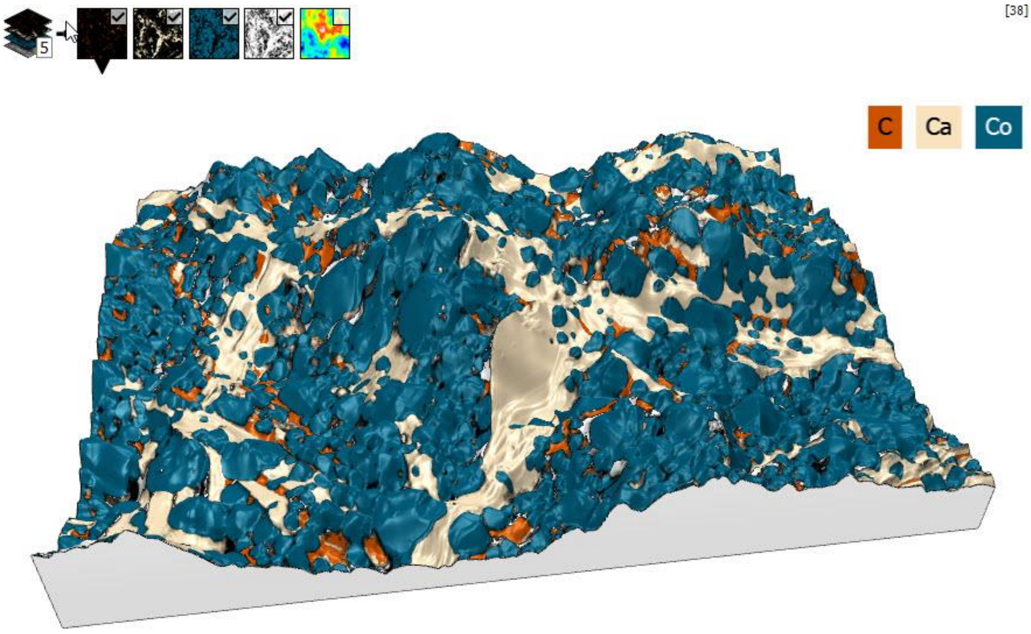

Figure 1: 3D model of surface topography generated from SEM images with overlay of chemical composition (EDS maps) on a Cobaltite sample.
Courtesy of Emmanuel Guilmeau, CRISMAT (Caen, France), Jean-Claude Ménard, JEOL France.

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A Fibre-Packaged Waveguide-Enhanced Raman Sensor

Waveguide-enhanced Raman spectroscopy (WERS) has attracted significant interest as a method leveraging the performance, size, and cost benefits of integrated photonics for Raman spectroscopic sensing of chemical and biological species [1]. While all the components of a full WERS system (light source, filters, interaction region, spectrometer) may eventually be integrated on a single chip, current limitations mandate using a source and spectrometer that are off-chip. The coupling of light to and from the WERS chip is most practically done using optical fibres, which can be bonded to the chip to remove the vibration sensitivity and need for expensive alignment stages inherent to lens coupling. Fibre-coupling however requires additional components to avoid the background from the fibres, notably a coupler separating the forward- and backward-propagating signals [2].

We present a fibre-packaged waveguide-enhanced Raman spectroscopic sensor with an adiabatic directional coupler enabling the collection of the backscattered signal and the removal of any signal from the fibres. Its limit of detection was quantified by measuring varying concentrations of isopropyl alcohol (IPA) in water. The signal-to-noise ratio (SNR) was calculated for each spectrum by normalizing the spectrum, subtracting a reference measurement of deionized water, and applying a penalized least squares algorithm to remove the baseline [3]. A fit of the evolution of the SNR with concentration suggests that the sensor's LoD for IPA lies at 0.03 mol.L^{-1} (0.2 wt% in water). This LoD is the lowest reported to date for a WERS sensor without surface enhancing mechanism.

References

[1] M. Ettabib, A. Marti, Z. Liu, B. Bowden, M. Zervas, P. Bartlett, and J. Wilkinson, "Waveguide Enhanced Raman Spectroscopy for Biosensing: A Review", ACS Sensors, vol. 6, pp. 2025-2045, 2021.
[2] D. Kita, J. Michon, and J. Hu, “A packaged, fiber-coupled waveguide-enhanced Raman spectroscopic sensor,” Optics Express, vol. 28, pp. 14 963–14 972, 2020.
[3] J. Ye et al. “Baseline correction method based on improved asymmetrically reweighted penalized least squares for Raman spectrum”, Applied Optics, vol. 59, pp. 10933-10943, 2020.

Figures

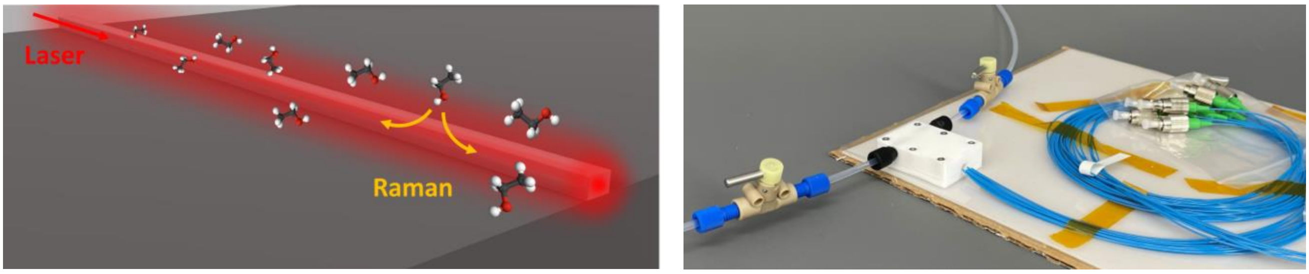

Figure: Schematic principle of WERS. A WERS sensor integrated in a flow cell for fluidic measurements.

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Ag-NPs decorated Vanadium Carbide MXenes hybrid film as efficient SERS Substrate for the sensing of Gemcitabine

Abstract

The 2D MXene materals have established the promising impact in the surface enhacned Raman spectroscopy (SERS) application. Due to excellent plasmonic and anti-fluorescent properties the Mxene could be a potential SERS substrate for the sensing of drugs. The AgNPs decorated vanadium carbide (V_2CT_x) MXenes has been proved to be excellent material due to its intermediate inter-layer spacing, short-range charge transfer (CT) and acting as Fermi level mediator between metal and drug fermi level. The numerous efforts have been madeto synthesize the V_2CTx materials with efficient inter layers space for better inter layer charge transtion and plasmonic effects. Herein, we report the synthesis and characterization of vanadium carbide sheets using environental friendly etchant (LiF+HCl). The fabricated multilayerd V_2CTx was delaminated with the novel intercalant triethylamine (TEA) which resulted in deceased interlayer spacing of 8.13 Å and enhanced the shelf life by up to six weeks. The prepared V_2CTx was treated with self-assembled silver nanoparticles (AgNPs) to fabricate the 2D hybrid materials as a potential SERS substrate for the sensing of ultra-trace quantities of anti-cancer drug gemcitabine (GMC). The developed analytical approach posed an unprecedented limit of detection of 10^{-12} M with a wide dynamic range of 10^{-4}-10^{-12} M. The AgNPs@ V_2CTx SERS sensor has achieved a Raman signal amplification corresponding to an enhancement factor of 10^9, with high sensitivity and reproducibility.

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Electronic band structure of Two-Dimensional Rhombohedral WSe_2 homobilayers

Twisted layers of atomically thin two-dimensional materials realize a broad range of novel quantum materials with engineered optical and transport phenomena arising from spin and valley degrees of freedom and strong electron correlations in hybridized interlayer bands[1,2]. Here, we report experimental and theoretical studies of WSe_2 homobilayers obtained in stable configurations of 2H (60° twist) and 3R (0° twist) stackings by controlled chemical vapor synthesis of high-quality large-area crystals[3,4,5]. We directly reported the electronic and structural properties of bilayer WSe_2 with the two stacking orders using micro-Photoluminescence (μ-PL) and micro-Raman spectroscopy, angle-resolved photoemission spectroscopy measurements (ARPES), and Density Functional Theory (DFT) calculations. Nano-ARPES clearly demonstrated that our bilayer with AB stacking shows a high spin-orbit coupling of about 500 meV. Our work opens up new perspectives in the development of optoelectronic and spintronic devices made of easily processable TMDs materials.

References
[1] Ruitao Lv et al. Acc. Chem. Res. 2015, 48 (1), 56–64.
[2] G. Wang et al, Rev. Mod. Phys. 90, 3721 (2018).
[3] Jiangang He, et al. Phys. Rev. B 89, 075409 (2014)
[4] Zhijie Li et al. Phys. Rev. B 106, 045411 (2022)
[5] K. M. McCreary et al. Nanoscale 14, 147 (2022).

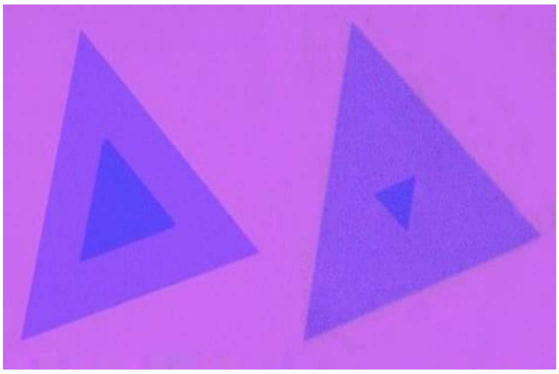

Figure 1: Optical image of CVD-grown WSe_2 bilayer flakes

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NanoMesureFrance: A single entry point for structuring the nanomaterials industry around reliable data

Nanomaterials are formidable sources of innovations and are used in all industrial sectors. However, their development is hampered by the fact that the reproducibility of industrial production processes is difficult to achieve [1], harmonised testing methodologies are lacking to implement their different regulatory definitions [2], regulatory requirements for which harmonised test methods are not always available and an often negative perception by society [3]. The lack of traceability [4] regarding the use of these chemical substances, the risks of which are sometimes still poorly assessed, and the fragmentation of French stakeholders do not favour the establishment of a context conducive to the marketing of products incorporating nanomaterials.

These various obstacles are partly due to the difficulties in obtaining reliable and comparable data, while the characterisation of nanomaterials is complex. In order to respond to these issues, this communication proposes to introduce the NanoMesureFrance initiative. This innovation centre, led by LNE and supported by the French State (via BPI, the French Public Investment Bank) and the Ile-de-France region for three years, aims to create a sustainable structure aiming at strengthening confidence in nanomaterials and associated innovations through improved quality characterisation data. NanoMesureFrance also aims to federate, within a non-profit association officially created in 2022, the French stakeholders concerned (nanomaterials producers & users, instrument manufacturers, service providers, laboratories and academic platforms) by working on the harmonisation and validation of the tools and methods needed to characterise key physico-chemical properties of nanomaterials at different stages of their life cycle. In addition to the creation of the NanoMesureFrance association, part (€1.5M) of the €2.8M budget for this project will be used to make the necessary investments to carry out the actions required to meet the specific needs discussed. The offer proposed within NanoMesureFrance will provide solutions adapted to the various levels of complexity and maturity of the problems expressed by its members. The latter will have access to a shared characterisation platform equipped with complementary instruments, to a range of high value-added services "around characterisation and testing" aggregating the capacities of the members, as well as to an Open Innovation programme conducive to the development, harmonisation and validation of innovative characterisation tools and methods in order to support the responsible industrialisation of nanomaterials and corresponding Safe-by-Design approaches. Beyond these actions, NanoMesureFrance will allow a better coordination of national efforts on these subjects and will defend French positions within European/international bodies and networks (European Metrology Network, OECD, VAMAS, AFNOR/X457, CEN/TC352, ISO/TC229).

References

[1] https://www.nanofabnet.net/
[2] https://ec.europa.eu/environment/chemicals/nanotech/review_en.htm
[3] https://echa.europa.eu/fr/-/what-do-eu-citizens-think-about-nanomaterials-
[4] https://www.anses.fr/fr/content/nanomat%C3%A9riaux-evaluation-du-dispositif-national-de-d%C3%A9claration-r-na

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Surface Enhanced Raman Scattering study of MXene based glass substrates

Surface Enhanced Raman Scattering (SERS) has become a powerful technique in the detection and identification of biologically important molecules. MXenes are a family of two-dimensional transition metal carbides and nitrides that exhibit plasmonic properties, making them promising candidates for the preparation of SERS active substrates. It has been shown previously, that MXene based SERS substrates are able to detect low concentration of organic dye molecules such as rhodamine B, rhodamine 6G, methylene blue, and crystal violet [1]–[3]. Nowadays, the applicability of detecting these molecules using MXene compounds has been extensively studied. However, there is still need to broaden their possible application to the detection of small concentrations of bio molecules. Here, we demonstrate the SERS properties of MXenes based glass substrates using rhodamine B, as a model molecule and study the possibility of using SERS enhancement for human insulin detection. We found that spray coated MXene continuous films on glass substrates exhibited SERS sensitivity. In particular, rhodamine B was detected in the range of 10^{-3} to 10^{-6} M. However, the substrates did not show SERS activity towards human insulin. The detection limit of insulin on the spray coated MXene on glass did not differ from bare glass substrate, being equal to 0.25 mM. Our results show that while MXenes are a very promising new SERS platform, further work is needed to utilize them in detecting small bio molecules at biologically relevant concentrations.

Acknowledgement: This work was supported by the Slovak Research and Development Agency under contract No. APVV-19-0465 and by the Slovak Grant Agency for Science under contract No. VEGA 2/0117/22.

[1] A. Sarycheva, T. Makaryan, K. Maleski, E. Satheeshkumar, A. Melikyan, H. Minassian, M. Yoshimura, and Y. Gogotsi, J. Phys. Chem. C, 121 (2017) 19983–19988
[2] S. Elumalai, J. R. Lombardi, and M. Yoshimura, Mater. Adv., 1 (2020) 146–152
[3] X. I. E. Xiaojing, Z. H. U. Yumei, L. I. Fang, Z. Xiaowei, and X. U. E. Tao, Sci. China Technol. Sci., 62 (2019) 1202–1209

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Detection of nanoparticles by surface-enhanced Raman microscopy

Nanoparticles are challenging to detect and image due to their size. While methods such as dynamic light scattering, nanoparticle tracking or scanning electron microscopy are commonly used to detect and determine the size of nanoparticles, either high concentrations are required or it is difficult to identify the type of particle that is detected.

Although Raman scattering is able to give information about the detected molecule, it is an inherently weak process, with only about one in 10^8 photons of the excitation beam contributing to the Raman signal. However, this signal can be enhanced by the excitation of surface plasmons on substrates like gold nanostructures.

Here, we show that by employing surface-enhanced Raman microscopy, we can enhance the Raman signal in such a way that single nanoparticles can be detected and by looking at the Raman fingerprint we can determine the type of nanoparticle that is observed.

Figures

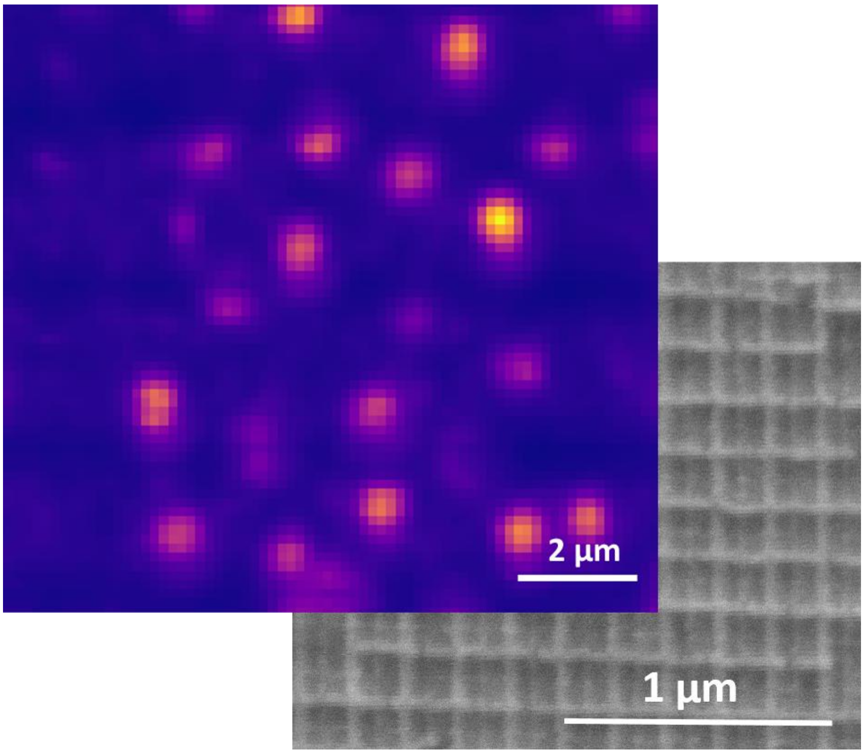

Figure 1: Surface-enhanced Raman substrate (right SEM image) and surface-enhanced Raman microscopy image (left) of polystyrene nanoparticles.

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Gold Flakes based nanostructure as new SERS sensing platform

Plasmonics, the physics of coupled states between light and surface charge density oscillations, is a thriving research topic with a plethora of potential applications, like miniaturized optical antennas, plasmonic waveguides, meta-materials, or high-sensitivity sensing [1]. Plasmonic nanostructures are often made from noble metals such as gold, as it is stable under ambient conditions and shows surface plasmon resonances in the visible wavelength range [2]. In this project, we utilized the gold flakes as highly efficient plasmonic structures platform (Fig.1). Plasmonic structures were fabricated by direct focused ion beam (FIB) milling [3]. The thin gold single-crystalline layer with an atomically smooth surface and structures demonstrated outstanding optical Raman signal enhancing compared to polycrystal gold (Figure.1). The results demonstrated that gold flake platform shows precise, reproducible, reusable, generic plasmonic substrate which has huge significance for basic science, pharmacological the agricultural and economy industries.

References

[1] Maier S. A., Springer (2007).
[2] Huang, JS., Callegari, V., Geisler, P. et al, Nat Commun1, 150 (2010).
[3] Coenen, T., Bernal Arango, F., Femius Koenderink, A. et al, Nat Commun 5, 3250 (2014).

Figures

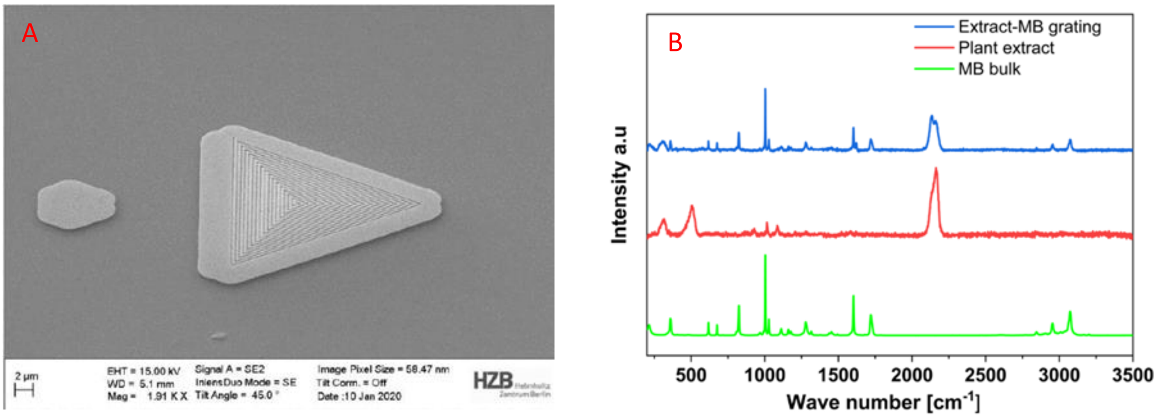

Figure 1: (A) Gold flake nanostructure milling, (B) Surface enhanced Raman signature obtained by gold nanostructures

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Characterization and harmonization for industrial standardization of advanced materials studied by Raman spectroscopy – The H2020 CHARISMA project

Raman spectroscopy is becoming a key technology used in research and development for characterization of materials. As such, any spectrum should be reliably comparable with any other and linked to specific material properties. However, in real life, Raman spectra can differ between instruments and depend on the spectrometer, optical path or sample environment, among others, and only a limited number of calibration standards for Raman spectroscopy are available to date [1].

The aim of H2020 CHARISMA project [2] is to develop new concepts to harmonize Raman spectroscopy for characterization across the life cycle of a material, from the product design and manufacture to lifetime performance and end-of-life stage. The main objectives are: development and production of universal, robust and readily available calibration standards and protocols for spectra acquisition and data analysis and storage; harmonization of raw Raman data through conversion to universal and open data format; generation of a FAIR [3] Raman data repository to enable exchange of spectral data between users. The project is based on strong cooperation between academic and industrial partners and is divided into a research-based technical part that will develop and analyze the tools, and the industrial part that will apply them in relevant case studies. It covers both experimental and theoretical Raman spectra generation, interpretation and storage following the FAIR principles. In the long term, CHARISMA aims to make Raman spectroscopy a widespread technology used within the Industry Commons concept.

References

[1] A. Ntziouni et al., Applied Spectroscopy 76 (2022) 747-772
[2] https://www.h2020charisma.eu/
[3] https://www.go-fair.org/fair-principles/

Acknowledgements

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Direct Correlative Nanoscopy Imaging of 2D Materials

2D transition metal dichalcogenides (TMDCs) materials are considered of very high potential semiconductors for future nanosized electronic and optoelectronic devices. An information-rich nanoscale characterization technique is required to qualify these materials and assist in the deployment of 2D material-based applications.

Scanning Probe Microscopy (SPM) is a powerful technique to image physical properties of 2D materials, such as topography, surface potential or other electrical properties. Combining SPM and Raman in a single instrumentation is extremely powerful as it makes imaging of both chemical and physical properties possible. As Raman is diffraction limited, only plasmon enhanced Raman and photoluminescence spectroscopies yield correlated electrical and chemical information down to the nanoscale.

In this poster, we will report on Tip-Enhanced Photoluminescence (TEPL) and Tip-Enhanced Raman spectroscopy (TERS) data obtained on single crystal TMDC flakes directly grown on SiO2/Si. TEPL and TERS images will be correlated with contact potential difference and capacitance maps as results of Kelvin force probe microscopy acquisition.

Beside these semiconductor/dielectric (SiO2) interfaces, probing TMDC/metal interfaces is also essential to integrate TMDCs in 2D or 3D complex structures of devices. We will show results from WS2 on silver and WSe2 and MoS2 on gold. Such transferred surfaces exhibit nanoscale inhomogeneities observed in correlated CPD and Raman maps.

Finally, TEPL together with AFM topography data on a lateral single layer WS2/WSxSe1-x/WSe2 heterostructure grown on SiO2/Si will be presented: nanoscale PL response variations are observed beyond the smooth nano-resolution topography.

References

[1]Nature Communications 9, 2891 (2018)
[2]The journal of physical chemistry letters, 11(15), 6112 (2020)
[3]Nature Nanotechnology 15, 854-86 (2020)
[4]Chem. Commun. 57, 6895 (2021)
[5]J. Phys. Chem. C 125, 48, 26883-26891(2021)
[6]J. Phys. Chem. Lett. 2022, 13, XXX, 5854-5859(2022)

Figures

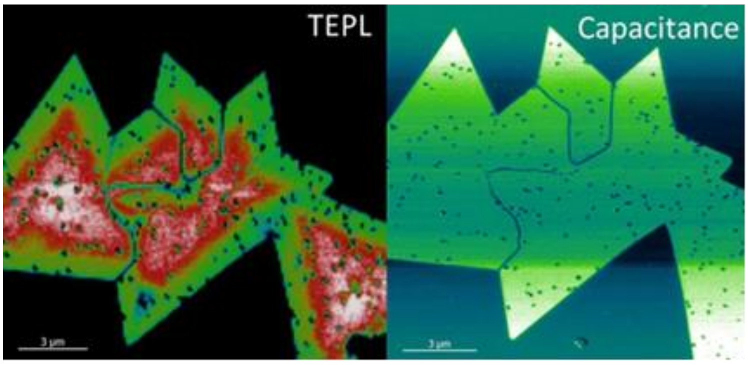

Figure 1: Correlated Tip-enhanced Photoluminescence and Capacitance measurements on WSe2 flakes

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Operando Raman Spectroscopy Investigations of the CO_2 Hydrogenation to Methanol on Cu-ZrO_2 based Nanocatalysts

The use of catalytic reactions to produce a large variety of valuable chemicals is a crucial process in the catalysis industry. In particular, the synthesis of methanol (CH_3OH) from the catalytic CO_2 hydrogenation reaction (CO_2 HR), $(CO_2 + 3H_2 \rightarrow CH_3OH + H_2O)$, has grown tremendously within the last few years, as it is an attractive approach to mitigate CO_2 by converting it into high value-added chemicals.

Within this framework we have conducted a comparative study of the CO_2 hydrogenation on two analogues nanocatalysts, the first in the form of mixed nanopowders of Cu-ZrO_2-ZnO-Al_2O_3 (CZZA), and the second consisting of ultrathin film of ZrO_2 grown on CuOx/Cu(111) surface. This comparative approach is intended to unravel the reaction mechanistic of the CO_2 HR. To this end, we have conducted operando Raman spectroscopy measurements using autoclave cells under realistic reaction conditions of the pressure (10-40 bar) and step-wise annealing from room temperature up to 400°C. Our study shows two major findings. The first concerns the reaction path followed during the CO_2 hydrogenation to methanol. It occurs via the reverse water gas shift mechanism (r-WGS). We have used isotopic labeling (D_2) to monitor the formation of D_2O specifically through the r-WGS process. Raman band shift of D_2O and other relevant intermediates such as CO, HDO were detected in the gas phase (Fig.). The second finding shows high catalytic performances of the ZrO_2/CuO_x/Cu(111) ultrathin film compared to the CZZA nanopowders. It is illustrated by the early onset of the r-WGS process which occurs at 100°C on the ZrO_2 films while it starts only at 200°C on the CZZA sample. Besides, the CO_2 conversion via the r-WGS is more efficient on the ZrO_2 films as it produces large amount of D_2O for less consumption of D_2 when compared to the CZZA sample. We attribute the better performances of the ZrO_2 ultrathin films to following effects: (i) the ZrO_2—CuOx/Cu interface where synergistic phenomena occur (CO_2 dissociation on ZrO_2 and D_2 dissociation on CuO_x), (ii) the unique role of the dual-reaction sites of ZrO_2, present in the ultrathin film, that are the strong Lewis acidity of Zr^{4+} cations and the strong Lewis basicity of both O^{2-} anions and oxygen vacancies (O_v) associated with Zr^{3+} states. We have evidenced the presence of these sites thanks to XPS investigations conducted on the ZrO_2 ultrathin films where the core-level spectra in the Zr binding energy region show the presence of two contributions, Zr^{4+} and Zr^{3+}.

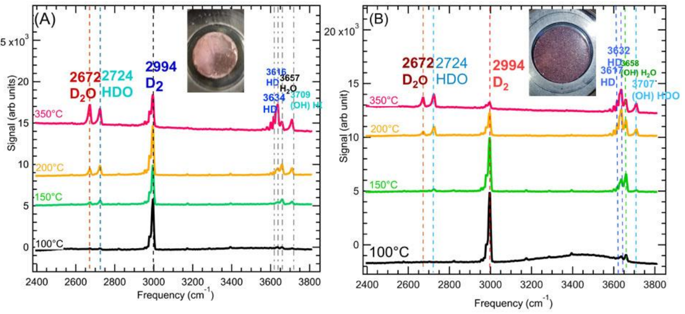

Figure: Operando Raman spectra as a function of the temperature for two nanocatalysts. (A): ultrathin film of ZrO_2 grown on CuOx/Cu(111) surface; (B) nanopowders of Cu-ZrO2-ZnO-Al2O3 (CZZA)

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