

	8:20-8:30	Opening Remark: Prof. Bin Ren		
<b>24<sup>th</sup> May</b> <b>(Room 202,</b> <b>Lujiaxi</b> <b>Building)</b>	8:30-9:10	<b>Prof. Johan Hofkens</b> The Power of One: What Can We Learn From Single Molecule Fluorescence Microscopy Measurements?	Chair: Prof. Xiaomei Yan	
	9:10-9:50	<b>Prof. Bin Ren</b> Electrochemical Raman spectroscopy towards the time and spatial limits		
	9:50-10:20	<b>Prof. Hiroshi Uji-i</b> Remote spectroscopy below the diffraction limit: Toward single cell interrogation		
	10:20-10:40	Coffee break		
	10:40-11:10	<b>Prof. Xiaomei Yan</b> High-Throughput Spectrochemical Sensing of Single Nanoparticles in a Sheathed Flow	Chair: Prof. Hiroshi Uji-i	
	11:10-11:30	<b>Dr. Gang Lv</b> Effect of Non-Metallic Nanostructures on Enhanced Raman Scattering		
	11:30-12:00	<b>Prof. Shoufa Han</b> Chemical probes for imaging and modulation of organelle functions		
	Lunch			
	14:30-15:00	<b>Prof. Maarten B.J. Roeffaers</b> Nano-imaging chemical properties of materials	Chair: Prof. Ye Yang	
	15:00-15:30	<b>Prof. Jianfeng Li</b> In-situ monitoring surface reaction process using SHINERS		
	15:30-15:50	<b>Dr. Haifeng Yuan</b> Surfaces, Boundaries, and Traps in Perovskite Nanocrystals		
	15:50-16:10	Coffee break		
	16:10-16:40	<b>Prof. Ye Yang</b> Surfaces Limit Carrier Lifetimes in Lead Halide Perovskite Films	Chair: Prof. Maarten B.J. Roeffaers	
	16:40-17:00	<b>Dr. Julian A. Steele</b> In Situ Raman analysis of Direct Laser Writing (DLW) of $\delta$ - to $\alpha$ -phase transformations in meta-stable perovskites		
Dinner (Lujiang hotel)				
<b>25<sup>th</sup> May</b> <b>(Room 215,</b> <b>Lujiaxi</b> <b>building)</b>	Panel discussion (8:30-11:00)	1. Belgium visit; 2. How to proceed the project; 3. Collaboration		
	Tour in Xiamen			

# Abstract

## The Power of One:

### What Can We Learn From Single Molecule Fluorescence Microscopy Measurements?

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Single molecule spectroscopy has tremendously impacted every field in which the technique was applied, ranging from catalysis over plasmonics, polymer physics, biophysics to cell biology and DNA sequencing. Furthermore, single molecule techniques have allowed researchers to push the resolution of fluorescence microscopy past the diffraction limit. In this presentation, I will give an overview of recent single molecule experiments in my laboratory. Progress in instrumentation, in polymer research (1), in plasmonics (2), in emissive silver clusters (3), in perovskite nano-particle research (4) and in DNA mapping (5) will be discussed.

#### References:

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- [4] H. Yuan et al J Phys Chem Lett 2016 7 (3) 561 ; J Steele ACS Nano 2017
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## Electrochemical Raman spectroscopy towards the time and spatial limits

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The electrochemical surface/interface determines the performance of electrodes. Normally there is only a monolayer or even sub monolayer of molecules that we are interested in on surface. Therefore, there is a growing demand for techniques to characterize the structure and electronic properties of catalysts on nanoscale. At present, it is still a great challenge for electrochemical characterization techniques to study electrochemical processes on surface/interface with higher sensitivity, temporal and spatial resolution.

We built an electrochemical microscope based on electrochemical surface enhanced Raman spectroscopy (EC-SERS). The spatially resolved EC information can be extracted via the localized EC faraday current of surface species reconstructed from the variation of SERS intensity during the EC reaction process. [1] To obtain the EC behavior of a single catalyst, we developed a dark-field spectroscopy based on the water-immersed objective, which can be for in-situ EC study. The sensitivity was significantly improved due to the absence of optical distortion. Here we studied the EC deposition process of silver on a single nanorod in situ. We developed EC tip enhanced Raman spectroscopy (EC-TERS), where the electronic level of the substrate and tip can be flexibly modulated with applied potentials, to observe the change of molecular structures on EC surface/interface. [2] The surface plasmon resonance (SPR) effect from the strong coupling between the tip and substrate enables the in-situ characterization of SPR catalysed reactions at nanoscale. Combined with modulation of applied potentials, we can further study the synergetic interplay of the SPR effect and applied potentials. Finally, we constructed a well-defined bimetal surface via under potential deposition of Pd islands on Au (111) surface. With the high spatial resolution of TERS imaging, we can characterize different sites on surface to illustrate the unique physicochemical property of the edge site by using phenyl isocyanide as a probe of surface electronic properties and catalytic features. [3]

### Acknowledgement

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## Remote spectroscopy below the diffraction limit: Toward single cell interrogation

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Metal nanowires can be used as wave-guides for propagating surface plasmon polaritons (SPPs), allowing the spatial confinement and transfer light energy over micrometer distance through the structures below sub-diffraction limited diameter. SPPs confined at the surface of single crystalline metal nanowires, such as wet-chemically synthesized silver nanowires, can propagate over tens of microns before energy is lost by Ohmic damping. Alternatively, the use of surface plasmons allows us to concentrate light energy in nanometer regions, such as a nanogap between metal nanoparticles, leading to a massive enhancement of electromagnetic field that can be used for surface enhanced Raman scattering (SERS) or fluorescence (SEF) spectroscopy/microscopy.

In this contribution, we introduce a noble nanoscopic techniques using a combination of these two concept, that of SERS/SEF detection of (bio)molecules and that of sub-diffraction limit SPPs wave-guiding. Specifically, we demonstrate that SPPs launched along a silver nanowire (50 ~ 100 nm diameter) can remotely excite SERS [1,2] and SEF [3] in the vicinity of the nanowire surface due to the SPPs wave-guiding effect. The ability to transfer SERS/SEF excitation over several microns, through sub-diffraction limited structures, will be discussed with respect to potential application toward super-resolution endoscopy [1] and tip-enhanced Raman microscopy [4].

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## High-Throughput Spectrochemical Sensing of Single Nanoparticles in a Sheathed Flow

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Ultrasensitive detection and characterization of nanoparticles (<100 nm) at the single-particle level is of great importance in biomedical research and nano-bio-technology development. Flow cytometry has been a well-established methodology for the rapid and multiparameter quantification of individual cells in suspension. Yet its sensitivity is far inferior to the analysis of single nanoparticles due to the fact that the scattered light intensity of nanoparticle scales off with the sixth-power of particle size, along with the minute amount of molecular contents enclosed. For example, a particle size decrease from 200 nm to 40 nm or 25 nm results in a signal reduction of 15,000-fold or 260,000-fold, respectively. Employing strategies for single molecule fluorescence detection in a sheathed flow, we have developed high sensitivity flow cytometry that facilitates light scattering detection of single extracellular vesicles, viruses, silica nanoparticle, and gold nanoparticles as small as 40 nm, 27 nm, 24 nm, and 7 nm in diameter, respectively. With a sizing resolution comparable to that of transmission electron microscopy (TEM) and the ease and speed of flow cytometric analysis, HSFCM is particularly suitable for nanoparticle size distribution analysis of polydisperse/heterogeneous/mixed samples. Moreover, through concurrent fluorescence detection, simultaneous insights into the biochemical properties of single nanoparticles can be achieved. Recent progresses in the multiparameter analysis of single viruses, extracellular vesicles, and nanomedicines will be reported.

### Acknowledgement

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## Effect of Non-Metallic Nanostructures on Enhanced Raman Scattering

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Surface-enhanced Raman scattering (SERS) have attracted much attention in physical, chemical and biomedical applications. Till now, the choice of SERS materials is limited mainly to metals, especially gold and silver for visible spectral excitation. On the contrary, non-metallic materials alone are believed not suitable for SERS due to the limited enhancement factor. They are usually used in SERS systems by forming a composite with SERS-active metal materials. However, in this composite, does the morphology of the non-metallic materials have an effect on the total Raman enhancement? This remains a question. Herein, we studied the effect of non-metallic nanostructures on SERS enhancement, and found that nanostructured non-metal materials, such as silicon, will introduce an additional Raman enhancement. Our finding will help to further understand the SERS mechanism and pave the way for making more efficient SERS systems.

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## Chemical probes for imaging and modulation of organelle functions

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Fluorescence imaging aided with advancing bio-targeting technologies provides unprecedented opportunities for spatiotemporal visualization of diverse biological processes at realms scaling from biomolecules to organelles and to whole organisms. [1] Lysosomes are acidic organelles essential to myriad cellular events including immunity, cell homeostasis, and cell death. [2] Abnormal lysosomes are manifested in numerous pathological conditions.[3] Cell fates are largely shaped by combined activity of distinct subcellular organelles, which are often targeted with synthetic probes driven by organelle parameters such as mitochondrial potentials and lysosomal acidity.[4] Albeit widely used, these probes are prone to dissipate upon organelle stress such as loss of lysosomal acidity. As such, approaches capable of continual tracking of stressed organelles are of use to decipher the roles of organelle biology and diseases.

Herein we present our efforts on the use of bi-functional probes to image dynamic lysosomes/mitochondria in cell stress. Particularly, organelle-specific glyco-probes, hijacking endogenous cell sugar sorting pathways, were harnessed for in vivo imaging of tumors and inflammation, and redirecting anti-tumor immunity via metabolic engineering of tumor cell surface glycocalyx.

### Acknowledgement

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## Nano-imaging chemical properties of materials

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Fluorescence microscopy is a recent addition to the toolbox for in situ study of solid catalytic materials. It combines ease of use with non-invasiveness, high sensitivity and temporal resolution.[1,2] Here we show how mapping of single catalytic turnovers yields nanoscale activity images of working catalysts.[3,4] By recording the fluorescence signal generated by every single catalytic conversions and by accurate image reconstruction, a nanoscale activity map can be generated. Overlaying such information on the corresponding electron micrographs, as obtained in a home-built integrated fluorescence-scanning electron microscope enables to precisely pinpoint the zones of enhanced catalytic activity. Next to significant intraparticle heterogeneities, the data also reveal important interparticle heterogeneities which have often been overlooked so far.

Besides heterogeneous catalysts also other advanced functional materials are investigated in my group such as photocatalysts[5] and perovskite materials for solar cell applications. Using the integrated fluorescence-electron microscopy we uncovered difference in current and light driven degradation processes in perovskites.[6] Moreover, we noticed particle-to-particle variations in perovskite degradation that could be linked to crystallinity. In another work we reported on the direct laser writing of the formamidinium lead iodide (FAPbI<sub>3</sub>) yellow  $\delta$ -phase into its high-temperature luminescent black  $\alpha$ -phase, a remarkably easy and scalable approach.[7]

### Acknowledgement

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## **In-situ monitoring surface reaction process using SHINERS**

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### **Abstract**

Surface-enhanced Raman scattering (SERS) can be used for in situ investigation of trace chemical species with fingerprint information. However, only a few noble metals such as Ag, Au, or Cu with roughened surfaces can generate strong SERS enhancement, which had limited practical applications. Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) was therefore invented to break the long-standing limitation of SERS. In SHINERS, Au/Ag core as plasmonic antenna provides high electromagnetic field to enhance targets' Raman signals, while ultra-thin, uniform and pinhole-free silica shell separates the Au/Ag cores from the system under study and ensures no interference from processes involving the SERS-active cores.

Shell-isolated nanoparticles (SHINs) can be spread as "smart dusts" over surfaces with diverse compositions and morphologies, and it has already been applied to a number of challenging systems, which can't be realized by traditional SERS. Combining with electrochemical methods, we have in-situ monitored the surface electro-oxidation at Au(hkl) electrodes, CO electro-oxidation, and oxygen reduction reaction at Pt(hkl) surfaces. Hydroxyl, peroxide and superoxide were directly observed as intermediates which proved the long-standing speculation in electrochemistry. On the other side, SHINERS-satellites strategy was also developed to in-situ monitor heterogeneous catalysis processes and their intermediates.

The concept of shell-isolated nanoparticle-enhancement is being applied to other spectroscopies such as fluorescence, IR, and SFG.

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## Surfaces, Boundaries, and Traps in Perovskite Nanocrystals

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Organic–inorganic halide perovskites (OIHPs) have demonstrated extraordinary energy conversion efficiency in solar cells and in light-emitting devices. Along with intensive developments in both materials and devices, surfaces, boundaries, traps and interfaces that significantly affect their device properties become recently an emerging topic. Here, we look into how the surface, boundaries and traps influence the material properties by the means of correlative optical and electron microscopy. By tuning the surface ligands, we demonstrate morphology and crystallinity engineering over solution-processed perovskite nanocrystals.[1] Furthermore, we utilize the integrated optical and electron microscopy to reveal the relationship between the material morphology and photoluminescence properties, showing that surface have important impact.[2] Particularly, we later focus on super-resolution localization microscopy for identifying and resolving the heterogeneously distributed traps.[3] Photo-active traps (PATs), that generate efficient non-radiative recombination channels, are mapped over OIHP nanocrystal morphology of different crystallinity. We determine the PAT density to be  $1.3 \times 10^{14}$  and  $8 \times 10^{13} \text{ cm}^{-3}$  for polycrystalline and for monocrystalline nanocrystals, respectively. The higher PAT density in polycrystalline nanocrystals is likely related to an increased structural defect density. Moreover, monocrystalline nanocrystals that are prepared in an oxygen- and moisture-free environment show a similar PAT density as that prepared at ambient conditions, excluding oxygen or moisture as chief causes of PATs. Hence, it is concluded that the PATs come from inherent structural defects in the material, which suggests that the PAT density can be reduced by improving crystalline quality of the material.

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## Surfaces Limit Carrier Lifetimes in Lead Halide Perovskite Films

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Organic-inorganic hybrid perovskites are attracting intense research effort due to their impressive performance in solar cells. Carrier recombination at defects is detrimental to the device performance. While the bulk carrier parameters in the perovskites such as mobility and bulk carrier lifetime show sufficient characteristics, the surface carrier dynamics has not been studied. If not properly managed, surfaces can be a major source of carrier recombination. Separating surface carrier dynamics from bulk and/or grain-boundary recombination in thin films is challenging. Here, we use transient reflection spectroscopy to investigate the surface carrier dynamics in both methylammonium lead halide perovskite single crystals and polycrystalline films.<sup>1-2</sup> We find that surface recombination limits the total carrier lifetime in perovskite polycrystalline thin films, meaning that recombination inside grains and/or at grain boundaries is less important than top and bottom surface recombination. The surface recombination velocity in polycrystalline films is nearly an order of magnitude smaller than that in single crystals, possibly due to unintended surface passivation of the films during synthesis.

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## **In Situ Raman analysis of Direct Laser Writing (DLW) of $\delta$ - to $\alpha$ -phase transformations in meta-stable perovskites**

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Most of today's technology in solar energy, telecommunications and microchips is constructed using silicon-based materials. However, in recent years, a new family of semiconducting materials, perovskites, has burst onto the scene, offering promise for new and better technologies. The properties of these materials rival many of the well-established commercial options, while remaining far cheaper and easier to make. One of these perovskites currently being investigated by researchers is formamidinium lead iodide [ $\text{HC}(\text{NH}_2)_2\text{PbI}_3$  or  $\text{FAPbI}_3$ ], which holds the world record performance for a perovskite-based solar cell, rivaling silicon-based ones. Important challenges, however, remain to be resolved regarding the stability of perovskite crystals under real-world conditions. At room temperature, for example,  $\text{FAPbI}_3$  arranges itself in the yellow coloured delta phase, with little practical value for technological applications. But when heated above  $150^\circ\text{C}$ , the material rearranges itself into a different black structure, called the alpha state, before reverting to the delta phase after a few days under ambient conditions. It is this dark alpha state of  $\text{FAPbI}_3$  that is most interesting for researchers and technology. Until recently, researchers have tried to access the high-temperature alpha state by heating the material and stabilizing it at room temperature using surface and chemical treatments. In this presentation, a novel way to create the sought-after dark alpha-phase perovskite will be outlined, using localized Raman laser heating to locally heat the crystal surface, making it change from the useless delta state to the highly desirable alpha state. Furthermore, materials optically processed in this way can be evaluated through studying the back-scattered Raman signals, providing deep insights into the optically-driven processes. The understanding developed from the in situ Raman studies allows for the precise tuning of laser-induced modifications, extending its applications to the rapid all-optical micro-fabrication of complex patterns of the dark  $\text{FAPbI}_3$  state.