

Congratulations to New ICFO PhD Graduate

Dr. Jana Ockova graduated with a thesis entitled ?Vibrations and energy transfer in molecules enhanced by single nanoantennas'

December 13, 2023

We congratulate Dr. Jana Ockova who defended her thesis today in ICFO's Auditorium.
Dr. Jana Ockova obtained her MSc in Chemistry at the University College of London. She joined the Molecular Nanophotonics research group at ICFO led by ICREA Prof. Dr. Niek van Hulst as a PhD student.
Dr. Ockova's thesis entitled ?Vibrations and energy transfer in molecules enhanced by single nanoantennas' was supervised by ICREA Prof. Dr. Niek van Hulst.

ABSTRACT:

Light is a powerful non invasive tool for probing matter down to its fundamental molecular properties. The past three decades saw advent of metallic nanoantennas engineered to concentrate light into sub diffraction limited hotspots and enhance optical properties of

nearby emitters by many orders of magnitude. This boosted optical microscopy, allowing it to interrogate even extremely dim systems at their most fundamental single molecule level. The enhancement and local confinement also unlocked sensing applications down to zeptomolar concentrations, which can revolutionise environmental monitoring, clinical diagnosis and personalised medicine. Beyond sensing, metallic nanoparticles can improve the efficiency of photovoltaic devices and next generation green catalysts. The current challenge for large scale practical implementations is lack of understanding and control of the underlying nanoscale processes. Here, we use optical microscopy and metallic nanoantennas to perform single molecule and single particle experiments to shed light on fundamental mechanism of photosynthesis, nanoscale parameters crucial for sensing and underlying photochemistry in nanoantenna hotspots relevant for catalysis.

Firstly, we employ gold nanorods and cryomicroscopy to study excitation energy transfer in the Fenna Matthews Olson photosynthetic complex. By probing one complex at a time at room temperature and 77 K, we uncover energy transfer between its subunits, where both experimental approaches constitute the first of their kind for this extremely dim system. Furthermore, we show that maximising the nanorod enhancement likely yields more efficient energy transfer to the nanorod than between the subunits of the complex, making them operate as effectively independent. Our results shed new light on the role of excitation transfer and annihilation in the regulation of photosynthesis.

Next, we evaluate Raman scattering enhancement of a library of ten nanoparticles using a home built automated Raman microscope. By recording a statistically significant dataset of spectral traces from discrete nanoscale spots, we can distinguish Raman enhancement performance of different types of nanoparticles that would otherwise appear identical in classical bulk measurements. Furthermore, adding a dark field scattering detection allows us to classify the measurements between single and multiple nanoparticles and directly probe the variability of single particle enhancements. This is a crucial parameter for sensing applications and the detailed nanoscale insight provided by our measurement platform can be used to accelerate the rational design of new nanoparticles for quantitative sensing.

Finally, we employ the automated Raman microscope to study light induced chemical reactions in metallic nanocavities. Specifically, we record surface enhanced Raman scattering of a few methylene blue molecules sandwiched between a gold mirror and a gold nanoparticle. We develop a new sample assembly compatible with oil immersion that yields a 150 fold increase in the molecular signal than previously published air coupling schemes. We use a pulsed laser to induce a chemical transformation of the methylene blue molecules. By interpreting the results in the context of plasmonic properties of the gold nanojunction obtained from dark field measurements and simulations, we were able to rule out lattice heating and narrow down the underlying mechanism to a plasmon induced sub picosecond process. Furthermore, we propose that spontaneous picosecond Raman spectroscopy is suitable to study reactions at metallic surfaces which lie at the heart of heterogeneous

catalysis.

Thesis Committee:

Prof. Dr. Maria F. Garcia-Parajo, ICFO

Prof. Dr. Emilie Wientjes, University of Wageningen

Dr. Eric Potma, University of California



Thesis Committee