

Two Balzan Research Projects

Federico Capasso

2016 Balzan Prize for Applied Photonics

Balzan GPC Adviser: Carlo Wyss

Project Supervisor: Federico Capasso

Researchers: Project 1: Miriam Serena Vitiello; Project 2: Margherita Maiuri

Affiliated Institutions: Project 1: Harvard School of Engineering and Applied Sciences, Harvard University, Cambridge MA; Project 2: Princeton University, Princeton, NJ; Polytechnic University of Milan

Period: 2017-

Federico Capasso is Robert Wallace Professor of Applied Physics and Vinton Hayes Senior Research Fellow in Electrical Engineering, Harvard School of Engineering and Applied Science, Cambridge, Massachusetts.

Two research projects have been undertaken by Federico Capasso's young researchers:

1. Optoelectronics and nano-photonics in two-dimensional nanomaterial heterostructures;
2. Quantum Effects in Complex Systems ('Q-EX').

Project 1: Optoelectronics and nano-photonics in two-dimensional nanomaterial heterostructures

Institution: Harvard School of Engineering and Applied Sciences, Harvard University, Cambridge MA

Supervisor: Prof. Federico Capasso

Proposed beneficiary: Dr. Miriam Serena Vitiello (CNR NANO - Nanoscience Institute, National Enterprise for Nanoscience and Nanotechnology (NEST), Scuola Normale Superiore, Pisa)

The project is based largely on Dr. Miriam Serena Vitiello's ideas, and aims to explore novel electronic, optoelectronic, and plasmonic phenomena in the 2D vdW

heterostructures, seeking device applications based on these nanoscale quantum structures.

Research will target radically new concepts and approaches to develop a novel optoelectronic technology based on 2D nanomaterials. All activities are driven by interdisciplinary methods and groundbreaking views, intersecting opto- and nano-electronics, photonics, materials science and quantum engineering.

Introduction

Artificial semiconductor heterostructures have played a pivotal role in modern electronic and photonic technologies, providing a highly effective means for the manipulation and control of carriers, from the visible to the Terahertz (THz) frequency range. Despite their exceptional versatility, they commonly require stringent epitaxial growth procedures due to the need for clean and abrupt interfaces, lattice matching or limited and controlled lattice mismatch, which proved to be major obstacles for the development of optoelectronic and photonic devices in the infrared.

The discovery of graphene has triggered an unprecedented interest in inorganic two-dimensional (2D) materials. Van der Waals (vdW) layered materials such as graphene, hexagonal boron nitride, transition metal dichalcogenides, and the more recently re-discovered black phosphorus (BP) display an exceptional technological potential for engineering nano-electronic and nano-photonic devices and components “by design”, offering a unique platform for devising heterostructures with a variety of properties. Each layer can indeed be forced to simultaneously act as the bulk material and the interface, reducing the amount of charge displacement within it. However, the charge transfers between different layers can be very large, meaning that large electric fields can be induced, therefore offering interesting possibilities for band-structure engineering.

Furthermore, these material systems also provide an intriguing platform for fundamental investigations, through the exploitation of their confined electronic systems.

Finally, being fully compatible with a wide range of substrates including flexible and transparent ones, if placed on chip with flat integrated optical circuits, they can allow maximal interaction with light, therefore optimally utilizing their novel and versatile

properties for a wealth of applications in transformational optics, optical communications, spintronics and high-resolution tomography.

A plethora of opportunities and novel functionalities can therefore appear when one starts to combine several 2D crystals in one vertical stack, allowing synergetic effects to become very important. The proposal aims to explore novel electronic, optoelectronic, and plasmonic phenomena in the 2D vdW heterostructures, seeking device applications based on these nanoscale quantum structures.

Summary of specific objectives:

- 1) Local investigation of the electronic and plasmonic properties of heterojunctions based on different 2D nanomaterials, developing novel scanning probe techniques in the far infrared, and specifically:
 - a) amplitude and phase sensitive near field microscopy with sub-10 nm spatial resolution;
 - b) near-field probes with integrated nanodetectors enabling large-area, high-resolution microscopy.
- 2) Development of novel nanoelectronic and photonic devices based on 2D nanomaterials and combined heterostructures.

Outlook and impact

The targeted goal of the proposal is to provide groundbreaking technological steps toward the development of a new technology based on 2D nanomaterials aiming to trigger the development of applications across the terahertz and the mid-infrared.

Ultimate electronics applications of the project's proposed research would include, for example, flexible electronic systems that utilize the superior mechanical pliability of vdW materials. The development of novel high-performance nanoscale optoelectronic components prospects great impacts on future emerging signal processing and computer technologies. These new capabilities can be heterogeneously integrated into silicon CMOS based electronics. Optical/optoelectronic applications include photodetectors and integrated photonic systems. The proposed work plan will also provide fundamental understanding of the materials properties and phenomena underpinning these applications. In addition, novel quantum electronic optoelectronic and nanophotonic devices have long been a focus in the device community because of

the improved power/bandwidth performance possible with optical links for communication.

Almost every new 2D material possesses unusual physical properties. The 2D physics in such materials is just starting to emerge. Still, the most interesting phenomena can be realized in van der Waals heterostructures, which now can be mechanically assembled or grown by a variety of techniques, prospecting the emergence of a new low cost technology that would finally also allow full tackling of the terahertz portion of the electromagnetic spectrum.

Summary of achieved results

1. Near-field probes with room-temperature nanodetectors for sub-wavelength resolution imaging

Near-field imaging with terahertz (THz) waves is emerging as a powerful technique for fundamental research in photonics and across physical and life sciences. However, in the THz spectral range (frequency: 0.3–10 THz, wavelength: 30–1000 μm) imaging is severely restricted by diffraction.

Spatial resolution beyond the diffraction limit can be achieved by collecting THz waves from an object through a small aperture placed in the near-field. However, light transmission through a sub-wavelength size aperture is fundamentally limited by the wave nature of light. To overcome the above limits, the team conceived a novel architecture that exploits the inherently strong evanescent THz field arising within the aperture, to mitigate the problem of vanishing transmission.

To this aim, they introduced a novel near-field probe architecture, where the evanescent THz field is converted into a detectable electrical signal at the nanoscale. The latter goal is achieved by integrating a THz nanodetector based on a thin flake of crystalline black phosphorus (BP) into the evanescent field region of a sub-wavelength aperture to enable efficient detection of the transmitted wave.

Their results pave the way to the development of new coherent THz microscopes for large-area sub-wavelength resolution phase- and amplitude-sensitive imaging. In combination with QCLs operating in the 1.5–5.0 THz range, this imaging technique can aid the development of novel optical components (mirrors, filters, metamaterials, metalenses and sub-wavelength resonators) and open new research avenues in the

studies of fundamental light-matter interaction phenomena in many interdisciplinary fields crossing optics, photonics, chemistry and biology.

Associated publications

O. Mitrofanov, L. Viti, E. Dardanis, M. C. Giordano, D. Ercolani, A. Politano, L. Sorba and M. S. Vitiello. “Near-field terahertz probes with room-temperature nanodetectors for sub-wavelength resolution imaging.” *Nature-Scientific Reports* 7, 44240 (2017).

2. Phase-resolved detector-less terahertz near-field microscopy

Scattering-type scanning near-field optical microscopy (s-SNOM) offers an exceptional potential for the nanoscale imaging of material properties, such as free carrier distribution, chemical composition, localization and propagation of plasmon, phonons and plasmon-polaritons and for capturing ultrafast dynamics in nanoscale systems. Amplitude and phase resolved s-SNOM thereby enables access to the spatial variation of complex-valued dielectric responses and both the amplitude and phase of near-field distributions.

THz frequency electromagnetic waves can resonantly interact with fundamental excitations of molecules and solids and thus offer an ideal tool for the optical characterization of emerging low-dimensional materials and biological systems.

In s-SNOM, an incident THz beam is focused on a sharp atomic force microscope (AFM) metallic tip strongly confining the THz radiation in the near-field region of its nanometric apex. Nanoscale resolved (10 - 100 nm) optical images can be retrieved by analysing the scattered THz radiation as a function of tip position, placing the tip in close proximity to the sample surface. Both amplitude and phase contrast information can be obtained by employing interferometric techniques. These methods, however, increase the complexity of the experimental arrangement by introducing additional optical components such as modulators, translators, beam splitters and, particularly, detectors, which, in the THz spectral range, usually rely on cryogenically cooled bolometric systems to retrieve the typically low intensity signals.

Progress in the field is therefore restricted by the lack of compact, room-temperature and fast detection systems and appropriate passive optical components for THz frequency operation.

During the first year of the Balzan proposal, the problem was tackled by conceiving a simple, potentially compact, detector-less s-SNOM system that operates in the self-detection (SD) mode. It features a THz QCL that senses the backscattered optical field through a voltage modulation induced inherently through the self-mixing technique.

To provide a proof-of-principle of the amplitude and phase contrast imaging capability of the SD-s-SNOM, a polar crystal (CsBr), which exhibits a strong phonon-polariton (Reststrahlen) resonance in the 2.2 – 3.3 THz range, was selected. This demonstrates amplitude-and-phase-resolved background-free SD-s-SNOM imaging with a spatial resolution comparable to the scattering tip size, providing a key step forward to make THz nanoscopy a widely used tool.

Finally, the capability of the team's SD-s-SNOM to image doped van der Waals layered materials was demonstrated. To this purpose, they selected hBN/graphene/hBN heterostructures and black phosphorus (BP), a technique which made it possible to unveil acoustic photons at THz frequencies in graphene, by capturing gate dependent s-SNOM signals in double-gated FETs and to determine carrier concentrations in Se-doped BP via optical contrast effects in the far-infrared.

Associated publications

M. C. Giordano, S. Mastel, C. Liewald, L. L. Columbo, M. Brambilla, L. Viti, A. Politano, K. Zhang, L. Li, A. G. Davies, E. H. Linfield, R. Hillenbrand, F. Keilmann, G. Scamarcio, and M. S. Vitiello. "Phase-resolved detector-less terahertz near-field microscopy" *Optics Express* 26, 18423 (2018).

3. Room-temperature Se-doped black phosphorus nanosensors at terahertz frequencies

Layered 2D materials, with a band gap, have recently triggered increasing scientific interest. Behaving like semiconductors, they only conduct electricity whenever the electrons absorb enough energy through heat, light, and other means. Depending on their specific band structures, these materials can disclose peculiar functionalities to be exploited for highly efficient light detection.

With an energy gap in between the gapless graphene and the larger gap transition-metal dichalcogenides, black phosphorus (BP) recently emerged as a fascinating and versatile material for photo-detection and plasmonic applications.

BP is composed of stacks of its monolayer structure, phosphorene, along the z-axis. Its band gap can be engineered and tuned by varying the number of layers stacked together. Unlike layered crystals with flat in-plane lattice, the BP monolayer, puckered along the armchair (x) direction, creates a fully anisotropic band structure that reflects in a large electrical and thermal in-plane anisotropy which can be nicely exploited to selectively design the detection dynamics from scratch.

Another feature that makes BP extremely interesting among 2D layered materials is its direct bandgap, dynamically tuneable via flake thickness control. This effect is evident for ultrathin flakes (<6 nm, 1 to 10 layers), whereas the bandgap saturates to about 0.3 eV above 20 layers (thickness >11 nm). However, despite these clear advantages, BP suffers from the lack of mechanical robustness and from a huge structural instability in ambient conditions. A stable fabrication procedure therefore requires under-vacuum encapsulation immediately after (or during) its mechanical exfoliation. This is a clear disadvantage for a practical implementation of photonic and nanoelectronic BP devices. Chemical doping of bulk black phosphorus is a well-recognized way to reduce surface oxidation and degradation.

Therefore, such a procedure was exploited to fabricate thermoelectric terahertz frequency detectors consisting of an antenna-coupled field-effect transistor (FET) exploiting an active channel, Se-doped BP flakes of different thicknesses. First, the thickness and crystalline quality of the exfoliated flakes were characterized. Then transport measurements were performed at room temperature (RT) in order to retrieve information about mobility (μ) and charge density (n). Finally, the THz photodetection performances of the devised detectors were measured.

The asymmetric feeding of THz radiation into the channel of a field effect transistor, which induces a THz-frequency field between the gate (G) and the source (S) electrodes, can enable RT THz detection via a number of different physical phenomena, depending on the orientation of the BP flake and of the device architecture. Specifically, since the longitudinal in-plane acoustic phonons show a sound speed (then a conductance) along the x-direction (4246 m/s) almost half than the sound speed along the y-direction (8397 m/s), FETs can detect THz radiation, very efficiently, by means of the thermoelectric effect as a consequence of the temperature gradient (ΔT) along the x-oriented BP channel, caused by the asymmetric feeding of the incident THz wave to the FET electrodes. Under this condition, a steady-state thermoelectric voltage $\Delta u_{SD} = \Delta T S_b$ (where S_b is the

Seebeck coefficient) develops across the channel. This voltage is proportional to the incident THz wave intensity.

The team's thermoelectric Se-doped BP detectors show a maximum room-temperature hole mobility of $1780 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in a SiO₂-encapsulated FET. Room-temperature responsivities of 3 V W^{-1} were reached, with a noise-equivalent power of $7 \text{ nW Hz}^{-1/2}$ at 3.4 THz, comparable with the state-of-the-art room-temperature photodetectors operating at the same frequency. The achieved results demonstrate that the inclusion of Se dopants in the growth process of black phosphorus crystals enables the optimization of the transport and optical performances of FETs in the far-infrared with a high potential for the development of BP-based electro-optical devices. The team also demonstrated that the flake thickness can be tuned according to the target application. Specifically, thicker flakes (>80 nm) are suitable for applications in which high mobility and high speed are essential; thinner flakes (<10 nm) are more appropriate for applications requiring high on/off current ratios, while efficient photodetection at THz frequencies can be reached with flakes 30–40 nm thick, due to the larger carrier density tunability.

Associated publications

L. Viti, A. Politano, K. Zhang and M. S. Vitiello “Thermoelectric terahertz photodetectors based on selenium-doped black phosphorus flakes” *Nanoscale*, 11, 1195 (2019).

4. Fast and sensitive terahertz detection using an antenna-integrated graphene pn-junction

Although the detection of light at terahertz (THz) frequencies is important for a large range of applications in the fields of medicine, security, quality testing, chemical spectroscopy and more, current detectors typically have several disadvantages in terms of sensitivity, speed, operating temperature, and spectral range.

A novel detector for terahertz radiation designed and developed to exploit the ability of graphene to efficiently convert absorbed light (of any wavelength) into hot graphene electrons. These hot electrons are subsequently responsible for creating a photoresponse through the thermoelectric effect. The team's novel, antenna-integrated THz photodetector design is based on high mobility, hexagonal BN (hBN)-encapsulated

graphene, with a device geometry that is explicitly designed towards exploiting the PTE effect.

Specifically, a dual-gated, dipolar antenna was employed to simultaneously create a pn-junction in a graphene channel located above the antenna, and concentrate the incoming radiation at this pn-junction, where the photoresponse is created.

The detector contains a dipole antenna that is located 15 nm below the graphene channel. The antenna consists of two branches that are separated by a very narrow gap, with a size on the order of 100 nm. This antenna gap serves for focusing the incoming THz radiation into a very small spot in the graphene channel. Here, the concentrated field of the antenna leads to (intraband) absorption and the subsequent creation of hot carriers. Since the creation of a photoresponse from hot carriers requires a gradient in the Seebeck coefficient, the antenna branches simultaneously as split gates were used. Appropriate voltages (V_L and V_R) are applied to the left and right antenna branch, and through capacitive coupling this creates a pn-junction in the graphene channel, and thereby a THz-induced photoresponse. Thus, the antenna simultaneously creates the photo-active area in the graphene channel (located around the pn-junction) and funnels incident radiation to this photo-active area, due to the very strong field enhancement of incident THz radiation above the gap between the two antenna branches. Compared to previous antenna-integrated, graphene-based THz detectors, the advantage of the team's design is that the antenna gap is much smaller (100 nm vs: several microns), which means that the THz intensity is greatly enhanced (four orders of magnitude). Also, there is no direct electrical connection between the antenna and the graphene, which means that there is no need for impedance matching to assure current flow between antenna and graphene.

Furthermore, hBN-encapsulated graphene was used, which leads to graphene with high mobility and low residual doping. This means that the resistance of the graphene channel will be low, and the system can be tuned relatively close to the Dirac point (point of lowest carrier density), where the Seebeck coefficient is largest. Finally, the graphene channel is patterned into an "H-shape" with a relatively narrow (micron-sized) width. The narrow width of the central part of the channel leads to an enhanced photoresponse, as the hot carriers will have a higher temperature. The wider sides of the graphene channel reduce overall device resistance by minimizing contact resistance.

The team demonstrates that this novel detector has excellent sensitivity, with a noise-equivalent power of $80 \text{ pW/Hz}^{1/2}$ at room temperature, a response time below 30 ns (setup-limited), a high dynamic range (linear power dependence over more than 3 orders of magnitude), and broadband operation (measured range 1.8-4.2 THz, antenna-limited), with the potential of being extended to significantly lower and higher frequencies using appropriate antennas).

Importantly, this detector simultaneously fulfills the requirements of room-temperature operation above 1 THz with short response time and $10 \text{ pW/Hz}^{1/2}$ -order noise-equivalent power, a combination that is currently missing in the state of the art.

In addition, it has the advantage of being based on low-cost materials with scalable integration capabilities with the well-established CMOS electronics for low-cost imaging systems. Furthermore, it is very low in power consumption, as it is a passive device.

Associated publications

S. Castilla, B. Terres, M. Autore, L. Viti, J. Li, A. Nikitin, I. Vangelidis, K. Watanabe, T. Taniguchi, El. Lidorikis, M. S. Vitiello, R. Hillenbrand, K. Tielrooij, F. H.L. Koppens. “Fast and sensitive terahertz detection using an antenna-integrated graphene pn-junction” *Nano Letters* 19, 2765 (2019).

5. Phase-sensitive terahertz imaging using room temperature near-field nanodetectors

Imaging applications in the terahertz (THz) frequency range are severely restricted by diffraction. Near-field scanning probe microscopy is commonly employed to enable mapping of the THz electromagnetic fields with sub-wavelength spatial resolution, allowing intriguing scientific phenomena to be explored, such as charge carrier dynamics in nanostructures and THz plasmon-polaritons in novel 2D materials and devices. High-resolution THz imaging, so far, has relied predominantly on THz detection techniques that require either an ultrafast laser or a cryogenically cooled THz detector.

The team demonstrated phase-sensitive near-field THz imaging at room temperature enabled by a simple and versatile interferometric optical setup with a THz quantum cascade laser (QCL) and an aperture-type near-field probe.

A nanowire (NW) thermoelectric sensor is integrated into the aperture, enabling subwavelength resolution and coherent gain for improved sensitivity. Thus the cost and complexity of the TDS system were eliminated by employing a THz QCL and a room-temperature detector, achieving phase-sensitive near-field imaging with sub-wavelength resolution. The imaging system architecture can be exploited with other coherent THz sources and a range of different nanoscale THz detectors.

Additionally, the same interferometric setup enables spectral analysis of the THz field. By performing phase-sensitive imaging of strongly confined THz fields created by plasmonic focusing, the potential of this novel architecture for high-sensitivity coherent THz imaging with subwavelength spatial resolution is demonstrated.

Associated publications

M. C. Giordano, L. Viti, O. Mitrofanov and M. S. Vitiello. “Phase-sensitive terahertz imaging using room-temperature near-field nanodetectors” *Optica* 5, 651 (2018).

6. Phase-resolved terahertz near-field nanoscopy of a topological insulator phonon-polariton mode

THz electromagnetic waves can be exploited to study fundamental light-matter interaction phenomena in a variety of systems such as molecules, solids and low-dimensional materials. Scattering-type scanning near-field optical microscopy (s-SNOM) has recently shown an intriguing potential for imaging of nano-materials with strongly sub-wavelength spatial resolution. In s-SNOM the electromagnetic radiation is efficiently focused at the apex of an atomic force microscopy (AFM) tip and optical near-field images can be retrieved with nanoscale spatial resolution by analyzing the radiation scattered from the tip. Despite the exceptional potential for mapping free carrier distribution, chemical composition, localization and propagation of plasmon, phonons and plasmon-polaritons and for capturing ultrafast dynamics in nanoscale-systems, s-SNOM at THz frequencies has been so far limited by available cryogenic and bulky sensitive THz photodetectors.

Amplitude- and phase-resolved near-field imaging is particularly appealing to enable access to the spatial variation of complex-valued dielectric responses of THz frequency resonant 2D materials, heterostructures and low dimensional systems. In this context, topological insulators (TIs) represent interesting materials to investigate, due to their

unique surface state properties and their recently unveiled potential for devising active THz photonic devices. The peculiar band structure of a TI indeed results in conducting surface states with an insulating behavior in the bulk, which offers the possibility to separately probe surface or bulk physics. Moreover, topological insulator surface states possess non-trivial features, inherited from their Dirac-like spectrum. Furthermore, TI offers many advantages: their optical and electronic properties can be engineered by playing with the material stoichiometry; with almost the same high-absorbance of graphene, they can exploit a tunable surface band gap; very importantly, the two-dimensional electron gas (2DEG) arising from the topological surface states (TSS) of three-dimensional TIs supports a collective excitation (Dirac plasmon) in the THz range.

The team demonstrated amplitude- and phase-resolved near-field imaging with 100 nm spatial resolution, of thin flakes of $\text{Bi}_2\text{Te}_{2.2}\text{Se}_{0.8}$, by exploiting a novel detectorless s-SNOM system based on a THz quantum cascade laser (QCL), operating in self-detection mode. The stoichiometry of the employed $\text{Bi}_2\text{Te}_{2.2}\text{Se}_{0.8}$ material has been engineered on purpose to have a Fermi level which only crosses the TSS Dirac cone, meaning that its TSS behave as an ideal 2D electron gas.

A $\text{Bi}_2\text{Te}_{2.2}\text{Se}_{0.8}$ phonon-polariton mode is expected to be at 2.3 THz (78 cm^{-1}). Therefore, the frequency of a single-mode, single plasmon THz QCL was progressively varied to excite the predicted phonon-polariton mode by means of the THz s-SNOM microscope operating in self-detection mode.

The backscattered optical field was then sensed by the QCL through a voltage modulation inherently induced through the self-mixing technique. A strong amplification of the near-field amplitude is detected at the higher harmonics of the signal when a single mode 2.3 THz QCL was funneled on the microscope tip. Conversely, a negligible amplitude contrast is unveiled when the TI material is excited with a 2.7 THz QCL. The s-SNOM interferometric system was then employed to directly measure the phase shift induced in the $\text{Bi}_2\text{Te}_{2.2}\text{Se}_{0.8}$ flakes, by exciting the 2.3 THz resonant phonon-polariton mode.

Associated publications

E.A.A. Pogna, L. Viti and M.S. Vitiello, under review.

Project 2: Quantum Effects in Complex Systems ('Q-EX')

Institution: Princeton University, Princeton, NJ; Polytechnic University of Milan

Supervisor: Federico Capasso

Proposed beneficiary: Dr. Margherita Maiuri (Chemistry, Princeton University, and Physics, Polytechnic University of Milan)

1. Ultrafast dynamics in bio-inspired molecular arrays

Organic small molecules, such as tetrapyrroles, play crucial roles in numerous processes in nature, serving as cofactors in proteins where they have several functions. For example, chlorophylls (which contain magnesium ions) are responsible for photosynthetic electron and energy transfer, whereas hemes (which are iron porphyrins) contribute to the transport of diatomic gases.

In the last two decades, a huge range of conjugated porphyrin arrays have been investigated, with the goal of synthesizing efficient bioinspired molecular systems for light harvesting, charge separation, or photocatalytic processes. Characterizing the photoinduced ultrafast processes involved in these molecules is necessary for understanding such processes.

This project exploits a series of zinc-porphyrin arrays recently synthesized, noncovalently linked through benzene-based hubs, with the aim of mimicking the structure and function of some chromophores in photosynthetic reaction centers. Compared to previous porphyrin arrays, the flexibility of the central hub allows the monomers to interact with each other via face-to-face π - π -stacking without any direct conjugation, making such systems excellent models for studying excitonic interactions in natural complexes such as those in bacterio-chlorophylls special pairs. Excitonic coupling of the porphyrin subunits is expected to activate additional excited state relaxation channels with respect to the monomer, which have not been observed so far.

The appearance of such supramolecular electronic interactions has been revealed, using ultrafast transient absorption spectroscopy with sub-25 fs time resolution. Upon photoexcitation of the Soret band, energy trapping within ~ 150 fs is resolved in a delocalized dark excitonic manifold. Moreover, excitonic interactions promote an additional fast internal conversion from the Q-band to the ground state with an efficiency of up to 60% in the hexamer. These relaxation pathways appear to be

common loss channels that limit the lifetime of the exciton states in noncovalently bound molecular aggregates.

Associated Publications

L. Moretti, B. Kudisch, Y. Terazono, A. Moore, T. A. Moore, D. Gust, G. Cerullo, G. D. Scholes, M. Maiuri. “Ultrafast Dynamics of Nonrigid Zinc-Porphyrin Arrays Mimicking the Photosynthetic ‘Special Pair’.” 11, 3443-3450, *J. Phys. Chem Lett.* (2020).

2. Excitonic interactions in 2D materials and their heterostructures

Atomically thin transition-metal dichalcogenides (TMDs) have come into the spotlight in optoelectronics thanks to their outstanding physical properties. Because of the strong quantum confinement effects, Coulomb interaction is poorly screened in single-layer (1L) TMDs, so that the excitons created by photo-excitation have large binding energy, up to several hundred meVs.

Among TMDs, MoS₂ has emerged as a promising candidate for the semiconducting analogue of graphene. While the steady-state properties of TMDs have been studied in detail by linear optical techniques, the recent application of time-resolved nonlinear spectroscopy has enabled the study of excited-state dynamics on femtosecond timescales, mainly employing ultrafast pump-probe spectroscopy. Although exciton dynamics in few- and monolayer TMDs have been largely studied in the past years, a complete understanding of the mechanisms leading to ultrafast exciton formation and couplings is far from being understood.

This project exploits ultrafast two-dimensional electronic spectroscopy (2DES) to unveil exciton dynamics in monolayer MoS₂. 2DES provides a more comprehensive picture of the excitonic response compared to pump-probe, since it gives simultaneous spectral and temporal resolution on the excitation and detection axes. By using a sequence of 3 pulses, 2DES improves over two-pulse pump-probe spectroscopy in its ability to map the full third-order optical susceptibility of a sample by correlating excitation and detection frequencies. Through this approach several physical insights have been achieved: direct measurements of the homogeneous/inhomogeneous broadenings, strong coherent interaction between excitons and trions, and signatures of biexcitons. Here the team reports broadband 2DES measurements on monolayer

MoS₂ at 77K and room temperature, using sub 20-fs broadband pulses resonant with both exciton transitions. The project's findings: (i) an ultrafast sub-50fs decay of the diagonal peaks due to optical exciton decoherence, dominated by inhomogeneous broadening and (ii) two cross-peaks relaxations feature, due to scattering towards dark exciton states, as predicted for MoSe₂ before.

A second follow-up project applied two-dimensional electronic spectroscopy (2DES) to study ultrafast processes in TMDs heterostructures (HS). In TMD-HS with type-II band alignment, interlayer charge transfer (ICT) occurs such that a hole and electron reside in different layers, resulting in an inter-layer exciton with a recombination lifetime at least an order of magnitude longer than intra-layer exciton recombination times. 2DES measurements of ICT in a WS₂/MoS₂ HS using sub-30 fs broadband pulses are presented. The team resolved hole-transfer from the MoS₂ layer on sub-20 fs timescales. Signatures of electron transfer are also present but are less well spectrally distinguished. Due to the broadband nature of this 2DES experiment the team additionally resolved dependence of the interlayer charge transfer rate on the energy difference between the electron or hole donating and accepting layers.

Associated publications

- M. Maiuri, S. Dal Conte, M. Russo, J. Wang G. Soavi, D. Dumcenco, A. Kis, A.C. Ferrari, G. Cerullo. "Excitonic Effects in Single Layer MoS₂ Probed by Broadband Two-dimensional Electronic Spectroscopy." 2019 Conference on Lasers and Electro-Optics (CLEO), San Jose, CA, USA, 2019, pp.1-2.
- V. R. Policht, M. Russo, F. Liu, C. Trovatiello, M. Maiuri, S. Dal Conte, X. Zhu, G. Cerullo "Observation of Interlayer Charge Transfer in Transition Metal Dichalcogenide Heterostructures via Time-resolved Two-Dimensional Electronic Spectroscopy." Manuscript in preparation.

3. Ultrafast broadband dichroism by transient optical symmetry breaking in plasmonic metasurfaces

Ultrafast nanophotonics is an emerging research area aimed at the development of nanodevices capable of light modulation with unprecedented speed. A promising approach exploits the optical nonlinearity of nanostructured materials, metallic or dielectric, to modulate their effective permittivity via interaction with intense ultrashort optical pulses. A variety of configurations has been reported and the

temporal dynamics following photoexcitation has been intensely investigated, both experimentally and theoretically. This is especially true for plasmonic nanostructures, where ultrashort optical pulses trigger a delayed third-order nonlinear response dictated by internal relaxation of the metallic nanosystems, allowing all-optical light modulation. While the ultrafast temporal dynamics following photoexcitation has been deeply investigated, subpicosecond spatial inhomogeneity occurring at the nanoscale has been so far neglected.

A current open challenge in manipulating ultrashort intense laser pulses remains the feasibility of all-optical modulation of light over a broad bandwidth, with a full recovery over an ultrafast subpicosecond timescale. Among the different kinds of all-optical functionalities, ultrafast polarization switching has recently attracted a huge interest for advanced applications in photonics and beyond. In this work, the team combines polarization-resolved pump-probe spectroscopy with a quantitative numerical model able to describe the ultrafast nanoscale inhomogeneities at very early times upon photoexcitation.

The rationale of this project is the following: prediction and observation that photoinduced spatio-temporal transients can break the symmetry of a plasmonic metasurface even if composed of highly symmetric metaatoms, thus generating a broadband dichroic response with ultrafast recovery of the initial isotropic configuration well before the complete relaxation of the nanostructure.

A plasmonic metasurface made of a square array of closely packed C4 symmetric gold nanocrosses with thickness $H = 45$ nm, width $W = 60$ nm and length $L = 165$ nm is considered. Such a symmetric nanomaterial provides a polarization independent static transmittance at normal incidence characterized by a broad dip around 800 nm, due to the degenerate longitudinal plasmonic resonances of the two arms of the nanocross and broadened by hybridization effects in the array. Such a degeneracy can be broken by the resonant absorption of an ultrashort pump pulse with linear polarization parallel to the direction of one of the arms. Photo-absorption creates a highly inhomogeneous near field, mostly because of the retardation-based nature of plasmonic resonances in relatively large nanostructures. The inhomogeneous absorption pattern in each metaatom locally affects the electronic population of gold, inducing a non-uniform out of equilibrium hot-carriers distribution which anisotropically modifies the metal permittivity. The fingerprint of the ultrafast pump-induced symmetry breaking is a transient transmission anisotropy, which can be revealed in a polarization-resolved

pump-probe experiment where the delayed probe pulse impinges at normal incidence with a linear polarization at 45 degrees to the nanocross arms.

A quantitative numerical model describes the ultrafast spatial transients in terms of three spatial and temporal variables specifying the internal energy dynamics in gold: the energy density stored in the non-thermal fraction of photoexcited carriers, the temperature of the thermalized population of hot electrons and the lattice temperature (which plays a minor role on the sub-picosecond time scales). These three variables are interlinked by a set of three coupled partial differential equations, referred to as the Inhomogeneous Three-Temperature Model (I3TM) which extends the popular 3TM, widely used so far for metallic and semiconducting nanostructures, by including the spatial dependence of the variables.

The team then employs finite-element method numerical analysis in the frequency domain to calculate the transmission spectrum of the metasurface at normal incidence for a linear polarization parallel and orthogonal to the pump, for a set of permittivity configurations obtained by sampling the gold permittivity distribution at different pump-probe delays. The difference of the relative differential transmittance for parallel and perpendicular probe polarizations results in a broadband ultrafast transient dichroism. The main contribution to the phenomenon arises from non-thermal carriers.

These theoretical predictions are compared with polarization resolved ultrafast pump-probe experiments. The metasurface is resonantly pumped by a 30-fs pulse at 850 nm and the relative differential transmittance is probed by a 10-fs visible pulse spanning the 565-735 nm wavelength range. A good agreement is retrieved both for the spectra and the dynamics of the pump-probe experiment.

This project has shown that photoexcitation of a plasmonic metasurface by an ultrashort optical pulse induces a transient symmetry breaking. Such spatio-temporal electronic transients at the nanoscale translate into an anisotropic local permittivity distribution, and subsequent ultrafast dichroic optical response of the metasurface, dominated by non-thermal hot-electrons dynamics. This modulation is broadband and returns to the isotropic configuration within few hundreds of fs. The project's results pave the way to all-optical control of light at Tera bit/s speed, with particular relevance for ultrafast polarization management.

Associated publications

A. Schirato*, M. Maiuri*, A. Toma, R. Proietti Zaccaria, P. Laporta, P. Nordlander, G. Cerullo, A. Alabastri, G. Della Valle. “Ultrafast Broadband Dichroism by Transient Optical Symmetry Breaking in Plasmonic Metasurfaces.” Submitted to *Nature Photonics*.

4. Plasmonic nanoparticle assemblies for light-activated drug release probed with ultrafast spectroscopy

Novel regenerative strategies aim to design advanced therapies for patients with severe or chronic diseases where body’s own response is not enough for the recovery of all functions. In the last years, researchers focused their attention on two strategies using biomaterials as carriers: i) stem cell-based technologies, ii) target/local delivery of specific drug and biomolecules (i.e., growth factors, cytokines). The major challenges of recent works are to improve drug loading, increase selectivity to target cells, and control the precise release of drugs.

This project focused on hydrogels, hydrophilic biocompatible three-dimensional networks, which found many applications in cartilage, central nervous system and bone repair strategies. Their mild gelling condition and elastic properties allow their use as carriers for drugs and cells at the same time. Indeed, by tuning their swelling properties, degradation rate and cross-linking density, it is possible to smartly control cell fate and release rates. However, the extremely good results obtained as cell carriers do not have the right corresponding in drug delivery applications both with hydrophobic and hydrophilic drugs. It is known that mechanisms involved in drug delivery through hydrogels are: i) Fickian diffusion, ii) swelling, and iii) degradation. This project aims to tune the swelling of the three-dimensional network in order to guarantee drug release only after a specific stimulus.

The team investigated the use of light irradiation of hydrogel networks to ameliorate the performances of a hydrogel library developed for cell-based therapies, obtained by synthesis from block polycondensation between agarose and carbomer, together with cross-linkers. To make such hydrogels light-responsive, gold-based nanoparticles (Au NPs) were physically entrapped within the hydrogel networks forming organic-inorganic composite materials. The ability of Au NPs to make organic networks sensible to light irradiation is well known in literature, and many research groups

described the promising possibility to load Au NPs within polymeric network to improve cancer treatment, antimicrobial activity, or bone regeneration.

The hybrid sample was studied as drug delivery system with and without light irradiation, both from experimental and modelling perspectives, loading composite hydrogels with a specific drug (dextran 70 kDa conjugated with fluorescein) that may mimic high steric hindrance therapeutic molecules like a wide class of proteins, such as antibodies or erythropoietin. The role of NPs PEGylation was widely studied for NPs colloidal stability while its influence in light-responsive induced materials is unexplored.

This project's results indicate that the use (or not) of PEGylation onto Au NPs can dramatically tune the final performance of the drug delivery devices, posing questions about the aggregation condition of the NPs in the gel. To unveil the physical mechanisms triggering the different drug release trends, ultrafast pump-probe spectroscopy was performed on the two classes of NPs-loaded hydrogel without any drugs to relate their photo-physics with the performances of the drug-loaded vehicles. By combining the ultrafast experiment with modeling, the project suggests a higher heat transfer efficiency of NPs aggregates respect to the isolated NPs, which supports the results retrieved from the drug delivery study.

Associated publications

L. Moretti, A. Rossetti, A. Mazzanti, L. Polito, F. Pizzetti, G. Della Valle, G. Cerullo, A. Sacchetti, F. Rossi, M. Maiuri. "Plasmonic Nanoparticles Assemblies Control Light-Activated Drug Release." Manuscript in preparation.

5. Ultrafast spectroscopy: state of the art and open challenges

The project supported the realization of a perspective article on ultrafast spectroscopy.

Ultrafast spectroscopy techniques use sequences of ultrashort light pulses (with femto- to attosecond durations) to study photoinduced dynamical processes in atoms, molecules, nanostructures, and solids. This field of research has experienced an impetuous growth in recent years, due to the technological progress in the generation of ultrashort light pulses and to the development of sophisticated spectroscopic techniques, which greatly increase the amount of information on the process under

study. This paper aims to provide a nonexhaustive overview of the state of the art of the field and point out future challenges. After first reviewing progress in ultrafast optics, which has enabled the generation of broadly tunable light pulses with duration down to a few optical cycles, the pump-probe technique is then discussed, showing examples of its capability to combine very high time resolution, down to the attosecond regime, with broad spectral coverage. Two-dimensional spectroscopy is introduced, and results that demonstrate the additional information content provided by the combination of temporal and spectral resolution are presented. After a review of the achievements of ultrafast X-ray and electron diffraction, which provide time-dependent structural information on photochemical processes, the article concludes with a critical analysis of the future open challenges in the field.

Associated publications

M. Maiuri, M. Garavelli, G. Cerullo. "Ultrafast Spectroscopy: State of the Art and Open Challenges" 142, 3-15 *Journal of the American Chemical Society* (2020).