Two Balzan Research Projects

Federico Capasso

2016 Balzan Prize for Applied Photonics

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Researchers: Project 1: Miriam Serena Vitiello; Project 2: Margherita Maiuri
Affiliated Institution: 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, material science and quantum engineering.

Introduction

Artificial semiconductor heterostructures 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 of 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 infared, 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 electrically controlled optical phase modulators with hBNgraphene/hBN.
3) 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 allow full tackling of also 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

1. 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. M. C. Giordano, L. Viti, O. Mitrofanov and M. S. Vitiello. "*Coherent near-field imaging at THz frequencies with enhanced sensitivity enabled,*" submitted to *Optica*.
3. M. C. Giordano, L.Viti, O. Mitrofanov, G. Scamarcio, S. Mastel, R. Hillenbrand, D. Ercolani, L. Sorba, and M. S. Vitiello. "Sub-wavelength near field imaging techniques at terahertz frequencies." *Quantum Sensing and Nano Electronics and Photonics XV,* 10540, 10540N (2018).

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 period 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/grahene/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," submitted to *Science Advances*.

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)

This project is inspired by the hypothesis that, if nuclear motion influences quantum dynamics of natural and bio-inspired molecular systems, it should be possible to extend the similar argument to the study of exciton dissociation in 2D materials and their hetero-structures. The key hypothesis of vibronically assisted charge separation in 2D heterostructures still lacks experimental evidence. Direct observation of the complex quantum dynamics at the 2D TMD interface will be one of the challenges of Q-EX project, with the outcome of generating important photo-physical insights and suggesting design principles for operation of ultrathin devices under non-equilibrium conditions.

Introduction

Recent advances of ultrafast laser spectroscopy have promoted deep studies of quantum effects in complex systems where excitons – correlated electron-hole pairs – play a central role in light-triggered dynamics. In the excitonic picture, the spatial extent of an electronic excited state is increased thanks to a coherent sharing of the excitation among subunits of the system. This quantum-mechanically coherent superposition of states evolves in time and, if strong, can be observed by spectral features that are perturbed, shifted, or split. These properties are determined by electronic coupling among the repeat units forming the material and strongly depend on the type of complex system involved.

Since these discoveries, the idea of quantum coherence in charge and energy transport has been extended and established from biology to a number of other photovoltaic materials and nanoscale systems. Particularly important are atomically thin two-dimensional materials, such as graphene and transition-metal dichalcogenides (TMD) MX2 (M = Mo or W, X = S, Se), which have come into the spotlight due to their outstanding physical properties. The extremely high carrier mobility of graphene and the tunable direct band gaps of TMDs highlight the crucial role that quantum confinement can have in producing several technologically relevant electronic properties.

Summary of specific objectives

Q-EX aims to explore the roles that nuclear motions play in the ultrafast exciton dissociation in two different complex systems, going beyond the framework of classical electron transfer Marcus theories. The project has two main objectives:

(a) the study of excitonic many-body effects in 2D materials and their heterostructures;
(b) the study of vibronic coupling in bio-inspired molecular arrays.

Summary of results

1. Excitonic Interactions in 2D Materials and their Heterostructures (Politecnico di Milano)

The extremely high carrier mobility of graphene and the tunable direct band gaps of TMDs highlight the crucial role that quantum confinement can have in producing several technologically relevant electronic properties. Due to the low dielectric constants and the strong quantum confinement effects, Coulomb force is poorly screened in single-layer TMD materials, so that the excitons created by photoexcitation have huge binding energy, up to 1 eV. In the single-layer (1L) limit, they exhibit an indirect-to-direct band gap transition, which is accompanied by efficient light emission in the NIR-visible range. In addition, the coupling of spin and valley degrees of freedom gives rise to valley-selective optical properties. TMDs offer also the exciting possibility of creating heterostructures, obtained by stacking one material on top of the other. Such systems, which are analogous to classical semiconductor heterostructures, display rich optoelectronic properties due to the bandgap mismatch of the different components.

During the first year of the project the team developed a multidimensional ultrafast optical technique, namely two-dimensional electronic spectroscopy (2DES) to understand the non-equilibrium optical properties of TMDs and their heterostructures. They are able to report one of the first 2DES measurements obtained on a 1L MoS2 sample, provided by collaborations with the Cambridge Graphene Center (Prof. Andrea C. Ferrari). 2DES is the elective tool for the experimental studies of this project, since it measures energy/electron transfers and electronic couplings in multi-absorbing systems. Thanks to its main advantage of providing simultaneously high temporal and spectral resolution, it is possible to disentangle spectrally congested features, such as the different electronic transitions in complex systems and many body effects.

In 2DES three consecutive incoming pulses, with two separate controllable delays impinge on a sample. This interaction creates a nonlinear polarization that emits a field from the sample, after a delay t. The emitted field can be fully resolved in amplitude and phase when it interferes with a fourth pulse (local oscillator) or with the third pulse by itself. By Fourier-transforming the signal with respect to the first tau and t at a fixed T delay, one can retrieve a 2D map as a function of excitation and detection frequency for a specific delay T. By correlating excitation·detection axes, it is possible to track the energy flow dynamics and detect electronic couplings between excited states.

Their preliminary results show three 2DES maps at specific T delays. These preliminary data, combined with deeper analysis and supported by calculation, might help to better understand the intricate ultrafast transient response in prototypical 1L TMD, such as bandgap renormalization and Coulomb exchange interactions. This is a crucial step before moving on to the study of the heterostructures.

Associated outcome

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* MoS_2 *probed by two-dimensional electronic spectroscopy.* Manuscript in preparation. Submitted to MRS Fall Meeting (2018).

2. Vibronic Coupling in Bio-Inspired Molecular Arrays (Princeton University)

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. Synthetic porphyrins are exploited for artificial light harvesting, ultrafast electron transfer in donor-acceptor complexes, and in organic solar cells. Characterizing the photoinduced ultrafast processes involved in these molecules is necessary for understanding such processes.

During the first phase of Q-EX project, Dr. Luca Moretti has been appointed as Visiting Associate Researcher at Princeton University to study the electronic interaction in artificial tetrapyrroles arrays. First results report on a comprehensive pump-probe investigation on recently synthetized arrays of zinc porphyrins (containing from two to six molecules) which have been shown strong excitonic interactions. The samples will be provided by Prof. Gust, Prof. Ana Moore, Prof. Tom Moore (Arizona State University).

Associated outcome

L. Moretti, B. Kudisch, Y. Terazono, A. Moore, T. A. Moore, D. Gust, G. Cerullo, G. D. Scholes, M. Maiuri. *Excitonic Effects in non-rigid Zinc-Porphyrin Arrays Studied by Sub-25 fs Near-UV Pulses,* manuscript in preparation. Contribution to ESP conference (2018).