

LIGHTinPARIS		Marie Skłodowska-Curie Actions Second call for COFUND PhD fellowships
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Selection Domain	EDOM (Waves and Matter)	
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PHD THESIS PROJECT		
ELIXIR2 - ExpLoring Indirect eXcitons in Innovative 2D semiconductoR hetero-nanostructuRes		
Summary / Abstract		
This project aims to investigate the photophysics of excitons in original assemblies and heterostructures of two-dimensional (2D) colloidal nanoplatelets. Using time-resolved Stark spectroscopy, we will investigate the dynamics of charge- and energy- transfer, exciton recombination and dissociation, while tuning the energy and coupling of the excitonic states. The dynamics will be probed by photoluminescence spectroscopy using a picosecond streak camera and femtosecond transient absorption spectroscopy. An important feedback between these measurements and the samples developed at ILM will be essential to obtain high quality interfaces and composition tunability. Principal 3i dimension: interdisciplinary Keywords • Nanophotonics (plasmonics, metamaterials, 2D materials, surfaces and interfaces, optomechanics) • Materials (inorganic, semiconductor, organic, liquid crystal, photochromics); 2D materials • Lasers • Ultrafast spectroscopy • Charge transfer • Exciton dissociation • Stark spectroscopy		

ELIXIR2 - ExpLoring Indirect eXcitons in Innovative 2D semiconductor hetero-nanostructuRes

Key Objectives

The ultimate objective of this project is to understand and drive efficient exciton dissociation into free charge carriers in heterostructures of ultrathin 2D semiconductor nanoplatelets (NPLs) of metal chalcogenides. These highly confined nanostructures, with a large absorption cross section and efficient transport properties, exhibit a strong exciton binding energy (of several 100s of meV), which is detrimental for charge separation in light-to-energy conversion devices. These NPLs provide an ideal platform to investigate the dynamics of charge transfer and exciton dissociation, with the undefined role of exciton delocalization, charge-transfer character and curvature-induced strain. These effects will be tuned through structural and interfacial design within 2D heterostructures with in-plane and out-of-plane geometries, and ultrafast Stark spectroscopy will be used to probe specifically the spectral and dynamical signatures of charge transfer excitons and their dissociation into free carriers.

Project

Context and state-of-the-art of Scientific Research project

Two-dimensional (2D) semiconductor nanostructures are very promising photoactive materials for various opto-electronic applications. These quantum well structures result in quasi-2D excitons with energy that is strongly thickness-dependent (quantum confinement) [1-3]. The development of colloidal nanoplatelets (NPLs), composed of only a few monolayers in thickness, opens a way to control their optical and electronic properties to a higher level while retaining a direct bandgap. They combine a giant oscillator strength [4] and efficient 2D transport [5,6]. However, the large exciton binding energy prevents natural exciton dissociation into free electrons and holes. Charge carrier separation before collection therefore only occurs at the interface with another material, for a high-energy offset. This leads to energy losses due to the smaller final potential between the lower energy hole and electron states. On the one hand, studies in-plane heterostructures remain highly limited due to the poor quality of their surface and interface, resulting in (ultra)fast charge trapping [7,8]. On the other hand, coupling of NPLs in out-of-plane assemblies is limited by the long chain ligands that ensure the 2D crystal structure and surface passivation. Gradient compositions and ligands exchanges are currently developed to face these issues, in particular by Benoît Mahler, at ILM Lyon.

Interestingly, more efficient exciton dissociation was reported in heterostructures presenting i) some charge transfer (CT) character in molecular systems [9], ii) polaronic effects (exciton localization through large coupling to optical phonons) in hybrid halide perovskite [10] and iii) curvature-induced strain in inorganic nanotubes [11]. We propose to study these three effects on NPL heterostructures, by varying the 2D exciton delocalization length with the NPL lateral size, tuning the electron- and hole- wavefunction overlap (CT character tuning) by external electric field and controlling the NPL geometry through ligand exchange as previously reported for homo-structures [12].

Importantly, the signature of trapped/localized excitons at the interface/surface defects often resembles to those of CT ones: low energy shifted emission correlated to a long lifetime. Absorption of CT excitonic transition is much weaker than those of direct excitons, which makes them difficult to study spectroscopically. However, due to their permanent dipole moment, CT excitons are strongly affected by electric fields. Yet, only a few attempts of Stark spectroscopy on colloidal homo-NPLs have been reported

[13,14]. In this project we combine synthetic methods and ultrafast Stark spectroscopy to study original and high-quality NPL heterostructures.

Description

ELIXIR2 project aims to underlying charge transfer and exciton dissociation, both processes involved in the conversion of light-to-electricity, within the next-generation of photoactive materials based on ultrathin 2D semiconductor nanostructures. In particular, the efficiency of such processes relies on the structural quality of the heterojunction within heterostructures composed of materials with a type II alignment of their energy levels. The resulting energy offset needs thus to be controlled, through the composition, quantum and dielectric confinement, but will also be tuned through external parameters such as electric fields (Stark effects).

Methodology: Colloidal synthesis of metal chalcogenide NPLs will be done at ILM. Core-crown NPLs (in-plane heterostructures) will be prepared following previous reports [15]. Gradient and alloy composition will be used to insure the epitaxial relationship at the interface. Original out-of-plane heterostructures with reduced inter-NPL distance will be developed [16]. For the devices, the nanostructures are sandwiched between two electrodes (at least one transparent as ITO), in a capacitor-like geometry, with a spacing allowing fields of 100s of kV/cm to be applied without high voltage.

We will use time-resolved photoluminescence (TR-PL) and femtosecond transient absorption (fs-TA), that are complementary: PL directly relates to exciton population in NPLs, while TA signals arise from exciton population, free charge carriers and any effect modifying the oscillator strength & frequency of the optical transitions. Excitation-fluence dependent measurements will disentangle single exciton dynamics from exciton-exciton recombination and possible non-geminate electron-hole recombination at long time (after exciton dissociation). It will also be used to estimate the exciton coherent length [17]. Change of PL intensity with temperature (from room- to cryo-) will be used to appreciate the change of radiative versus nonradiative lifetime. Effect of external electric fields will be investigated for both TR-PL and TA measurements, to characterize the classical and non-classical Stark effect in the dynamics.

Bibliography

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Facilities and quality of research environment available for the researcher

Ultrafast laboratory at LuMIn (access 100%): Amplified TiSa laser source (Astrella, Coherent) ; Home-made visible non collinear optical parametric amplifier (NOPA); Home-made fs-TA (temporal resolution 40 fs, dynamics up to >3.2 ns, shot-to-shot detection); Time-resolved PL in reflection with a picosecond streak camera (Optronis) coupled to a spectrograph (temporal resolution about 5 ps, dynamics up to 2 ns); LN₂/LHe cryostat for measurements down to 77 K/4 K; Waveform generator (up to 10 V); Lock-in amplifier.

Characterization laboratory at LuMIn: UV-visible-NIR spectrophotometer for linear absorption; IR spectrometer; Fluorimeter for PL and PL excitation, fluorescence anisotropy, options: integrated sphere, time-correlated single photon counting (temporal resolution <0.5 ns, dynamics up to μs) with tunable excitation rate.

The PhD student will be performing time-resolved Stark spectroscopy measurements on the currently developed (and funded) ultrafast setups. She/he will be trained on the optical techniques by E. Cassette. She/he will benefit from the research group/lab environments of Physicists and Chemists, eventual (mechanical or electrical) support from the Physics department of ENS Paris-Saclay and from the rich scientific environment of Paris-Saclay University.

Chemistry laboratory at ILM: The partner built a colloidal synthesis laboratory comprising dedicated facilities for air sensitive chemistry (Schlenk lines, glove box), semiconducting nanocrystals synthesis (controlled heating and precursors injection setups), purification (centrifuges) and characterizations: luminescence and absorption spectroscopy (possibly in-situ), X-ray diffraction and Raman/IR spectroscopies. Electron microscopy imaging can be carried out either in-house or using the CLYM platform, including a high-resolution scanningTEM microscope (Jeol NeoArm ColdFEG).

Security training in Chemistry and for laser use will be provided at both LuMIn and ILM.

3i Dimension - interdisciplinary

Description and expected outcomes

The electronic and optical properties of semiconductor nanostructures are highly dependent on their size, shape and composition, which are thus essential to control. Colloidal synthesis enable the engineering of nanostructures with such precision and over a wide range of tunability. Ultrafast optical spectroscopy is an ideal tool to investigate exciton recombination, charge transfer and trapping dynamics in colloidal nanostructures, either dispersed in organic solvents, or embedded within solid-state matrices that are typically needed in opto-electronic devices. Furthermore, it can be used to study specific collective effects arising from inter-exciton or inter-particle interactions. Importantly, all these photo-physical properties can be used as a feedback loop to iteratively guide the chemical synthesis and design of specifically engineered hetero-nanostructures and assemblies. Specifically, these are two specific questions we aim to address by combining our interdisciplinary expertise: 1) How can we engineer CT excitons within out-of-plane heterostructures, which formation is typically prevented by the long, insulating surface ligands? For this, we need to master ligand exchange while preserving good surface passivation, quantum confinement and stable crystalline structures. 2) How can we obtain samples with all NPLs having a specific orientation (for Stark spectroscopy)? We will work on the protocol of NPL deposition on substrate or on the mechanical properties of the polymer used as matrix. Fluorescence anisotropy will be used to characterize the NPL orientation.

Approximate timeline of internships / external stays corresponding to the 3i dimension

The goal of the stays at ILM Lyon will be first to synthesize colloidal NPLs (homo- or in-plane hetero-nanostructures) within well established protocols (some are already reported). New synthesis are currently being developed at ILM with full chemist students, under the supervision of B. Mahler. The PhD student will be interacting closely with them during her/his stays. Then, the PhD student will take time to learn and develop ligand exchange protocols, nanoplatelets assemblies and rolling, as well with the preparation of the devices needed for Stark spectroscopy measurements.

The stays will be organized as follow, for a total of 12 weeks:

- Year 1: Spring 2027: 3 weeks, Autumn 2027: 3 weeks
- Year 2: Spring 2028: 2 weeks, Autumn 2029: 2 weeks
- Year 3: Spring 2029: 2 weeks

Each stay will involve a round trip by train from Massy/Paris to Lyon that will be paid by the research groups (LuMIn mostly) and the apart-hotel for the 2/3 weeks + living expenses for a maximum of 5.400 euros in total (450 euros/week). This will be financially covered by the 150 euros/months travel allowance already included in the salary of the PhD student, thanks to the LIGHTHinPARIS fellowship. Any (inter)national conference attended by the PhD student during the project will be funded by the PI (other research grant/funding).

Profile of PhD fellow

PhD studies and research work require curiosity, creativity, rigour, teamwork, and organisational skills. A minimum B2 level of English is mandatory. The below criteria are specific to the thesis project.

pre-requisite	Master's degree in Physics or Physical Chemistry, with an academic background in Quantum Mechanics, Solid-State Physics and Material Science.
pre-requisite	Experience on exciton photophysics or working on optical spectroscopy
pre-requisite	Knowledge in basic programming (Python, ...)
advantageous	Experience working with optical setups
advantageous	Experience working at the interface with Materials Chemistry.

Ethics issues in the project as per Horizon Europe Ethics Self-assessment

Section 1. Human embryonic stem cells (hESCs) and human embryos (hEs)			No
Section 2. Humans	No	Section 3. Human cells and tissues	No
Section 4. Personal data	No	Section 5. Animals	No
Section 6. Third Countries	No	Section 7. Environment, health and safety	Yes
Section 8. Artificial Intelligence	No	Section 9. Other ethics issues	No
Section 10. Crosscutting issue: potential misuse of results			No

7. Environment, health and safety

Laser safety (laser class 4 in the visible/near-IR), chemical safety (organic solvents & nanomaterials), cryogenic temperature. All French labs are required to have health and safety procedures in place, which takes into account the use of high-energy light sources such as lasers of class 3 and above, and the use of hazardous / toxic chemicals. The institution and the laboratory comply with the highest safety requirements and PhD fellows have mandatory health and safety training, with additional training if required.