SORBONNE UNIVERSITÉ

Sorbonne Université/ China Scholarship Council program 2020

Thesis proposal

Title of the research project: **Optoelectronic properties investigations in perovskite nanostructures of "the new generation"**

Keywords: **Perovskite colloidal nanocrystals, semiconducting nanostructures, opto-electronic properties, optical and magneto-optical spectroscopies, spin relaxation, spin coherence.**

Joint supervision: **NO**

Joint PhD (cotutelle): **NO**

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Institution: **Sorbonne Université and CNRS**

Doctoral school (N°+name): **ED PIF 564 *Physique en Île-de-France***

Research laboratory: **Institut des NanoSciences de Paris – INSP UMR 7588**

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Avis favorable de l'ED 564

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SORBONNE UNIVERSITÉ

Subject description:

1) Study context

Fully inorganic lead halide perovskites currently attract great attention due to several promising optoelectronic device applications in fields that span from photovoltaic solar cells to light-emitting diodes and lasers. Some of them are already used as the new generation of phosphors in industrial applications and integrated in displays [1]. Their intrinsic properties also make them strongly attractive for quantum technologies with demonstrations that have already confirmed their huge potential [2].

The 3D hybrid perovskites whose archetype is $CH_3NH_3PbI_3$ (MAPI) have recently created a spectacular breakthrough in the field of photovoltaics as an absorber material. Hybrid perovskite cells achieved a record yield of 25.2 % in 2019 after only a few years of development [3]. This spectacular breakthrough is due to electronic properties particularly well suited for photovoltaic applications: a band gap in the near infrared, a high absorption coefficient, and low excitonic effects at room temperature. In addition, the hybrid perovskites are prepared in solution at room temperature, which is interesting for the production of solar cells at low cost.

There is therefore a real need for studies that tackle the underlying basic electronic processes from which many applications arise. The aim of the thesis is thus to unveil the fundamental optoelectronic properties of perovskite materials tailored at the nanometric scale under the forms of all-inorganic colloidal dots and 2D bulk-like organic-inorganic (hydrid) structures.

2) Details of the proposal

Emission properties of $CsPbX_3$ (X=Cl, Br, I) colloidal nanocrystals

The all-inorganic, halide based perovskite nanocrystals (p-NCs) are considered as the new generation of semiconducting emitters [2]. Produced by easy colloidal synthesis they have indeed emerged as an interesting alternative to material-based II-VI NCs which have monopolized the attention of researchers over the last twenty years. They combine enhanced absorption cross-section, a bright room temperature (RT) photoluminescence (PL) with reduced blinking as well as a high PL efficiency (up to 90%) without requiring surface shelling thanks to a defect tolerant band structure. This key breakthrough in the field of colloidal NCs has led to a sky-rocketing scientific interest in these NCs. Moreover, the substitution of the halogen atom, X, and the variation of the confinement through the p-NC size allow tuning the emission wavelength from the ultraviolet to near-infrared.

In this context, fundamental studies are more than ever required to gain a perfect knowledge of the emission details conditioned by the band edge exciton fine structure that is currently debated. This is therefore one of the goals of this part of the Thesis project to determine the importance of the parameters ruling the energetic hierarchy of the band edge excitons states and their nature emitting or not: spatial and dielectric confinements, spin-orbit coupling (SOC), crystalline structure, shape anisotropy [4-8].

The emission properties mainly of a *single* nanocrystal addressed individually using a micro-photoluminescence set-up will be studied. The spatial and dielectric confinements will be varied with the size, shape and composition of the synthetized nanocrystals in the laboratory. The emission properties of these new materials will be investigated by continuous-wave and time-resolved spectroscopies. Dynamics of the emission and so lifetimes will be explored from low to room temperature. The single photon source nature of a nanocrystal will be tested with increasing temperature in anti-bunching experiments.

Spin relaxation in perovskite nanostructures: from thin films to p-NCs

The potential of perovskites for spintronics applications has just begun to be investigated. The presence of a Rashba-type splitting in the conduction band of hybrid perovskite has recently been predicted [9]. The strong SOC allows a good spin injection but a large SOC can also severely limit the spin relaxation lifetimes. Few studies on spin coherence in perovskite bulk-like hybrid films has been published [10, 11]. Fundamental understanding of spin-dependent physics in perovskites is still absent, such as accurate description of the spin polarized states and spin relaxation processes. While on one hand, possessing a large SOC, on the other hand. Detailed studies on elucidating the spin dynamics and decoherence as well as understanding the dominant relaxation mechanisms are thus needed to assess the material suitability for spin-based applications.

We aim at building a realistic image of spin properties, from bulk materials under the form of high quality monocrystalline films towards 0D p-NCs where enhanced protection against decoherence is expected. Time resolved magneto-optical experiments will be conducted to measure spin lifetimes and extract the exciton Landé factors. The relaxation properties and magneto-optical transient responses will be studied with increasing confinement and correlated to the Zeeman couplings induced by the magnetic field inside the exciton manifold. The investigation in this part of the project will require the previous deep understanding of the band edge exciton fine structure as well as its evolution with the dimensionality of the considered systems as described above.

Studies will thus start on mono-oriented films in which experimental conditions, as far as symmetry is concerned, and hence magneto-optical coupling can be easily controlled unlike the case of dots where effects of the dot orientation may be more difficult to handle. Temperature dependence of the spin lifetime will finally provide insights into the spin relaxation mechanisms.

The proposed studies are thus rather of fundamental nature. They allow gaining insights into the mechanisms that determine the intrinsic basic electronic and spin properties of single or interacting confined systems. The syntheses of the various perovskite quantum dots are currently carried out at INSP and the high crystallographic quality films are elaborated by national collaborators [12-13]. Let us note that a novel experimental platform allowing dots and films studies but also micro-PL measurements on individual p-NCs or local transient spectroscopies under magnetic field up to 5 Teslas at cryogenic temperatures has been developed specially for the project of the PhD Thesis.

Techniques involved: Micro-photoluminescence, magneto-micro-photoluminescence, time-resolved luminescence, pump-probe configuration spectroscopy (Time Resolved Faraday Rotation), low temperatures studies using cryogenic setup, absorption spectroscopy, design of experimental systems (work in clean room, spin-coating, electrode deposition, etc).

3) References (in blue references from the host team)

[1] X. Zhao *et al.*, “Opportunities and Challenges in Perovskite Light-Emitting Devices”, *ACS Photonics* 5, 3866 (2018).

[2] F. Hu *et al.*, “Superior Optical Properties of Perovskite Nanocrystals as Single Photon Emitters”, *ACS Nano* 9, 12410 (2015).

[3] NREL Chart http://www.nrel.gov/ncpv/images/efficiency_chart.jpg

[4] Ramade J. *et al.* “Exciton-phonon coupling in a $CsPBBr_3$ single nanocrystal”, *Appl. Phys. Lett.* 112, 072104 (2018).

[5] Ramade J. *et al.* “Fine structure of excitons and electron-hole exchange energy in polymorphic $CsPbBr_3$ single nanocrystals”, *Nanoscale* 10, 6393 (2018).

[6] R. Ben Aich *et al*. “Bright-Exciton Splittings in Inorganic Cesium Lead Halide Perovskite Nanocrystals”, *Phys. Rev. Applied* 11, 034042 (2019).

[7] M. Baronowski *et al.* “Giant Fine Structure Splitting of the Bright Exciton in a Bulk $MAPbBr_3$ Single Crystal”, *Nano Lett.* 19, 7054-7061 (2019).

[8] R. Ben Aich *et al.* “Multiband k·p Model for Tetragonal Crystals: Application to Hybrid Halide Perovskite Nanocrystals”, *J. Phys. Chem. Lett.* 11, 808 (2020).

[9] The Rashba effect appears when there is no inversion symmetry and leads to spin splitting of electronic states in absence of an applied magnetic field. M. Kepenekian *et al.*, “Rashba and Dresselhaus Effects in Hybrid Organic-Inorganic Perovskites: From Basics to Devices”, *ACS Nano* 9,

11557 (2015).
[10] D. Giovanni *et al.*, "Highly Spin-Polarized Carrier Dynamics and Ultralarge Photoinduced Magnetization in $CH_3NH_3PbI_3$ Perovskite Thin Films", *Nano Lett.* 15, 1553 (2016).
[11] P. Odenthal *et al.*, "Spin-polarized exciton quantum beating in hybrid organic–inorganic perovskites", *Nat. Phys.* 13, 894 (2017).
[12] H. Diab *et al.*, "Narrow Linewidth Excitonic Emission in Organic−Inorganic Lead Iodide Perovskite Single Crystals", *J. Phys. Chem. Lett.* 7, 5093 (2016).
[13] F. Lédée et *al.*, "Fast growth of monocrystalline thin films of 2D layered hybrid perovskite", Cryst. Eng. Comm. 19, 2598 (2017).

4°) Profile of the Applicant (skills/diploma…)

The applicant must have a master degree in Physics. Will have a taste for experimental work and a strong background in semiconductor physics, condensed matter, light- condensed matter interaction and eventually magnetic field-nanostructures interaction. Taste and/or skills in nanocrystal colloidal synthesis will be appreciated.

Contacts:

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