Campagne 2020 Contrats Doctoraux Instituts/Initiatives

Proposition de Projet de Recherche Doctoral (PRD)

Appel à projet IMat - Institut des Matériaux 2020

Intitulé du Projet de Recherche Doctoral : Elucidating interplay, stability and charge transfer dynamics at lead halide perovskite nanocrystal / 2D transition metal dichalcogenide interface for solar cells applications.

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Unité de Recherche :
Intitulé : Institut des Nanosciences de Paris
Code *(ex. UMR xxxx)* : UMR7588

Ecole Doctorale de rattachement de l'équipe & d'inscription du doctorant : **ED397-Physique Chimie des Matériaux**

Doctorants actuellement encadrés par le directeur de thèse (préciser le nombre de doctorants, leur année de 1ere inscription et la quotité d'encadrement) : 1 doctorant en seconde année 100%

Co-encadrant :

NOM : Prénom :
Titre : Choisissez un élément : ou HDR ☐
e-mail :

Unité de Recherche :
Intitulé :
Code *(ex. UMR xxxx)* :

Ecole Doctorale de rattachement : **Choisissez un élément :** Ou si ED non Alliance SU :

Doctorants actuellement encadrés par le co-directeur de thèse (préciser le nombre de doctorants, leur année de 1ere inscription et la quotité d'encadrement) :

Cotutelle internationale : ☒ Non ☐ Oui, précisez Pays et Université :

Description du projet de recherche doctoral *(en français ou en anglais)*

3 pages maximum – interligne simple – Ce texte sera diffusé en ligne

Détailler le contexte, l'objectif scientifique, la justification de l'approche scientifique ainsi que l'adéquation à l'initiative/l'Institut.
Le cas échéant, préciser le rôle de chaque encadrant ainsi que les compétences scientifiques apportées. Indiquer les publications/productions des encadrants en lien avec le projet.

Préciser le profil d'étudiant(e) recherché.

Merci de nommer votre fichier pdf :
«ACRONYME de l'institut/initiative_2_NOM Porteur Projet_2020 »

à envoyer simultanément par e-mail à l'ED de rattachement et au programme :
cd_instituts_et_initiatives@listes.upmc.fr avant le 30 mars.

Elucidating interplay, stability and charge transfer dynamics at lead halide perovskite nanocrystal / 2D transition metal dichalcogenide interface for solar cells applications.

The project is proposed at Institut des Nanosciences de Paris in the team "Physico-chimie et dynamique des surfaces" under the supervision of Nadine Witkowski and in collaboration with E. Lhuillier for the synthesis of nanocrystals. The project aims at developing a new method of deposition of nanocrystals using electro-spray and building a comprehensive understanding of lead halide perovskite nanocrystal and 2D dichalcogenide materials electronic structure and their interplay.

1) Study context and objectives

Defect tolerant nanocrystals (NCs) representing lead halide perovskite lattice (PeNCs) have recently been demonstrated to display remarkable photoluminescence (PL) efficiency up to 90% while offering notable colour purity in comparison with that of organic dye molecules [Protesescu2015]. Owing to their exceptional optical properties, PeNCs are promising candidates for highly efficient photovoltaic devices using PeNCs with optical gap covering the sun spectrum in a simple design.

Solar cells are produced by stacking functional layers, with adapted energy band levels, to absorb photons and maximize the extraction and separation of positive and negative charges (see Fig. 1). In such stack, the resulting power conversion efficiency depends not only on the light harvesting material (PeNCs) but also on the ability of transport layers to extract charges effectively. In this context, the optimization of a solar cell device strongly depends on both the intrinsic nanocrystal opto-electronic properties and their interaction with the transport layers. While the proof of concept for solar cells based on PeNCs was recently demonstrated [Swankar2016] using spin-coating deposition, the performance lifetime of devices are limited by their sensitivity to external stresses such as temperature / moisture / radiation that affects both PeNCs absorbent materials and the transport layers. It is then crucial to propose alternative materials used in combination with PeNCs to improve the device stability while keeping excellent performances.

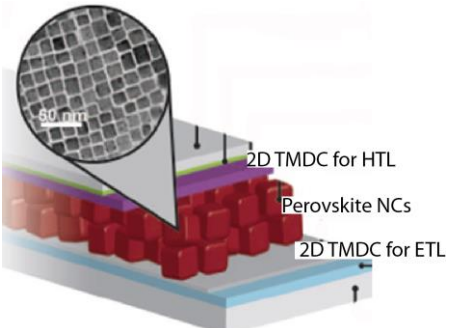

Fig. 1: Solar cell architecture, illustration adapted from ref.[Swankar2016]

In such context, the goal of the present project is to explore the route to replace sensitive charge transport materials with 2D transition metal dichalcogenide materials (TMDC) that combine excellent transport properties with higher stability. The focus will be put on deciphering the fundamental mechanisms that govern the charge transfer and dynamics at interfaces, by building a comprehensive understanding of PeNCs and 2D dichalcogenide materials electronic structure and their interactions at interfaces. In the perspective of long term stability, the interplay with temperature / moisture / radiation will be thoroughly investigated to unveil the mechanisms that can affect the performances of the device based on these advanced materials and propose strategies to minimize their effects. For such purpose, a radically new method of deposition of PeNCs using electro-spray will be developed, allowing in situ deposition and characterization without exposing samples to atmosphere environment.

Expected objectives and results include:

1. Characterizing electronic structure, energy band alignment and charge transport of PeNCs layers produced using electro-spray.
2. Elucidating interface interaction, charge transfer dynamics of PeNCs / 2D TMDC interface on model systems and selecting the most promising system for device development.
3. Understanding the effect of external stresses such as radiation / temperature / moisture on the electronic structure of PeNCs and 2D TMDC

2) Scientific approach

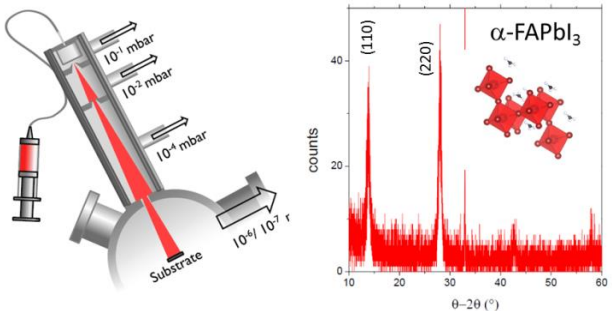

Figure 2 : Left : sketch of electro-spray ; right : XRD on FAPbI3 nanocrystal using electro-spray deposition at INSP

PeNCs are able to produce high photo-luminescence efficiency through straightforward and reliable synthesis. Recently, such new concept for solar cells has raised the efficiency to 16.6% in late 2018, approaching bulk crystal lead halide perovskite solar cell record. However, device processing requires several steps difficult to control (atmospheric spin-coating deposition, ligand exchanges). Moreover, the effectiveness of such devices may be limited by the transport of charges within the film due to the difficulty to control the interface with surrounding charge transport layers.

To overcome the difficulty induced by processing, we propose to explore a **radically new method** for the deposition of PeNCs **by electro-spray** under vacuum (see Fig. 2), allowing solution processing in perfectly controlled conditions. An electro-spray has been recently successfully used at INSP in the "Physico-chimie et dynamique des surfaces " team, to produce PeNCs layers whose crystallographic structure, composition and electronic structure are similar to PeNCs films obtained by standard spin coating deposition (see Fig. 2).

In standard solar cell architectures (see Fig.3) the absorbent is surrounded with electron and hole extracting layers consisting of TiO_2 (ETL) and MoO_3 (HTL) respectively that hold appropriate energy levels to split the exciton at the interface. In the case of PeNCs, the electronic structure and composition at the interface is strongly modified by the oxide that has led to use Spiro-OMeTAD ($C_{81}H_{68}N_4O_8$), an organic macromolecule, that displays very good performances as a hole transport material. However, it has its own drawbacks such as performance deterioration at high temperatures (above 60°C) and need of dopant [Miyasaka2018]. The idea in the present project consists in studying 2D transition metal dichalcogenide as a buffer layer between PeNCs and oxide layers to improve the performances and reliability of the modules [Wang2019]. Indeed, TMDCs possess large charge carrier capabilities and stabilities and offer a large variety of composition for use in high-performance solar cells. Recently, TiS_2 has been incorporated as electron transport layer, in 2D perovskite solar cells processed by spin-coating showing efficiencies of ~18 % [Huang2018]. Recent calculations have shown that WSe_2 should possess appropriate energy levels to act as a very efficient charge buffer layer [Xu2018]. However, currently only limited work has been done on the characterization of band alignement and electronic structure at the interface between perovskite and TMDCs and none regarding nanocrystals of lead halide perovskite, calling for a fundamental investigation of energetic band alignement and stability at interfaces PeNCs/TMDCs.

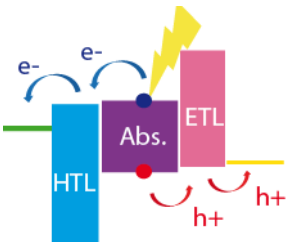

Figure 3 : Energy band alignment in n-i-p solar cell

Photoemission on the valence band using ultra-violet radiation (UV) is the ideal tool to address band alignment because it gives a complete picture of the valence states and work function of the PeNCs and TMDCs. In a complementary way, core level photoemission using X radiation (X-ray) can inform on the changes occurring in the oxidation states at interfaces PeNCs/TMDC. Modification of electronic levels at interfaces under stresses such as temperature/ radiation/ moisture will be investigated on the set-up recently installed in the team allowing both in situ deposition and characterization. Standard measurements including X-ray diffraction, FTIR, AFM/KPFM, UV-visible absorption, transport measurements will be done at INSP to characterize physical properties of PeNCs. The investigation carried out at INSP will be supplemented with advanced techniques using synchrotron radiation to investigate the dynamics of charge transfer at interfaces with time-resolved photoemission [Amelot2020] and the reactivity to atmospheric gases with Near-Ambient Pressure X-ray photoemission. Experiments using Time-resolved two-photon photoemission (TR-2PPE) have also already been requested to Nanosciences Foundries and Fine Analysis in Trieste (NFFA) to study the

relaxation dynamics of the excited states in PeNCs layers produced by electro-spray that induces diffusion, localization and recombination of carriers.
Moreover, the project aims at exploiting facilities offered at INSP with the equipment of a new set-up for the growth of 2D TMDCs that will be used as substrate for spray deposition of PeNCs. As a prospective of the project, smart inks of 2D TMDCs will be explored using spray deposition compatible with cost-effective large production of solar cells in collaboration with Prof. Xinliang Feng from Technical University in Dresden.

3) Details of the proposal and applicant skills

The PeNCs of choice is formamidinium lead iodine (FAPbI3), already produced in the team and studied using spin-coating deposition [Amelot2020], it is the most stable PeNC available to date. Single crystals of TiS_2 and WSe_2 will be used as model systems to study the interplay between PeNCs/TMDC.
During the first year, the PhD candidate will be trained during three months to vacuum technologies, spray deposition, electron spectroscopies and other experimental techniques available in the lab. The PhD candidate will then characterize physical properties such as electronic structure, energy band alignment, charge transport, structure, compositions, optical properties of PeNCs layers produced using electro-spray and compare the influence of deposition methods (spin coating vs. spray).
During the second year, the interplay and stability at PeNCs/TMDC interfaces will be investigated by means of electron spectroscopies. Particular attention will be focused on the charge transfer during operation that will be the subject of a proposal for beamtime at BESSY and SOLEIL synchrotrons using pump probe experiments with a laser. The stability toward external stresses of 2D TMDC materials and PeNC will be also investigated.
During the third year, the PhD candidate will work on the monolayer system either exfoliated from single crystals or grown in situ. Indeed, part of the team is already involved in a Graphene Flagship project LAMES aiming at growing monolayers of XS_2 materials (X= transition metal) and the project will benefit from the new infrastructure under development at INSP to grow XSe_2 materials (X=transition metals). Other samples will be purchased for the needs of the project.
The recruited PhD candidate will hold a master or equivalent in solid state physics, material physics, nanophysics or equivalent with a strong background in condensed matter physics. Knowledge of deposition techniques by spin coating/and/or vacuum depositions will be appreciated. Female applicants are strongly encouraged to apply.

4) Adequacy with priorities at Institut de Sciences des Matériaux

The present project revolves around studying nano and low dimensional materials for energy that are in the scope of the 2020 Institut de Science des Matériaux call. In this project, we propose an original way for the deposition of PeNCs that is expected to help for the development of all solution process for further technological application at large scale. This way of deposition has never been explored so far for PeNCs and preliminary results show that $FAPbI_3$ nanocrystals are promising nanomaterials for the development of cost-effective solar cells. Moreover, the project will benefit from infra-structures under development at INSP for the elaboration of 2D TMDC for charge transport layers.

5) References (bold from the team and collaborators)

[Protesescu2015] L. Protesescu, et al., Nano Lett. 15, 3692-3696 (2015) DOI: 10.1021/nl5048779
[Swankar2016] A. Swankar, et al., Science 354, 92–95 (2016) DOI: 10.1126/science.aag2700
[Miyasaka2018] A. K. Jena et al, J. Mater. Chem. A 6, 2219 (2018) DOI: 10.1039/c7ta07674f
[Amelot2020] D. Amelot, et al , J. Phys. Chem. C (2020), 124, 6, 3873-3880 https://doi.org/10.1021/acs.jpcc.9b10946
[Wang2019] B. Wang et al. Chem. Soc. Rev. 48, 4854 (2019) DOI: 10.1039/c9cs00254e
[Huang2018] P. Huang et al. ACS Appl. Mater. Interfaces 10, 14796-14802 (2018) https://doi.org/10.1021/acsami.8b03225
[Xu2018] K. Xu et al., Phys.Chem.Chem.Phys. 20, 30351 (2018) DOI: 10.1039/c8cp05522j