

**PROGRAMME INSTITUTS ET
INITIATIVES**

Appel à projet – campagne 2021

Proposition de projet de recherche doctoral (PRD)

iMAT - Institut de Science des Matériaux

Intitulé du projet de recherche doctoral (PRD): Nanocrystal-based micro-lasers for biological sensing

Directrice ou directeur de thèse porteuse ou porteur du projet (titulaire d'une HDR) :

NOM : PONS Prénom : Thomas
Titre : Chargé de Recherche ou
e-mail : thomas.pons@espci.fr
Adresse professionnelle : LPEM - 10, rue Vauquelin - 75005 Paris
(site, adresse, bât., bureau)

Unité de Recherche :

Intitulé : Laboratoire de Physique et Etude des Matériaux
Code (ex. UMR xxxx) : UMR8213

École Doctorale de rattachement de l'équipe (future école doctorale de la doctorante ou du doctorant) : ED397-Physique Chimie des Matériaux

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1^e inscription et la quotité d'encadrement) : 4

Alexandra Bogicevic, 2018-2021, 50%; Subha Jana, 2018-2021, 100%; Fanny Delille, 2019-2022, 50%; Yuzhou Pu, 2020-2023, 100%

Co-encadrante ou co-encadrant :

NOM : Maitre Prénom : Agnès
Titre : Professeur des Universités ou HDR
e-mail : agnes.maitre@insp.upmc.fr

Unité de Recherche :

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

École Doctorale de rattachement : ED564-Physique en IdF



Ou si ED non Alliance SU :

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1^e inscription et la quotité d'encadrement) : 3

Damien Simonot (2020, 100%)

Arnaud Choux (2017, 100%, fin de rédaction)

Xingyu Yang (2020, 50%)

Co-encadrante ou co-encadrant :

NOM :

Titre : Choisissez un élément : ou
e-mail :

Prénom :

HDR

Unité de Recherche :

Intitulé :

Code (ex. UMR xxxx) :

Choisissez un élément :

École Doctorale de rattachement :

Ou si ED non Alliance SU :

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1^e inscription et la quotité d'encadrement) :

Cotutelle internationale : Non Oui, précisez Pays et Université :

Selon vous, ce projet est-il susceptible d'intéresser une autre Initiative ou un autre Institut ?

Non Oui, précisez Choisissez l'institut ou l'initiative :

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

Ce texte sera diffusé en ligne : il ne doit pas excéder 3 pages et est écrit en interligne simple.

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.

The development of integrated light micro-sources is aimed in particular at miniaturization and integration with other micro-optical/electronic components. In this context, micro-lasers are a promising source for developing applications ranging from quantum photonics to new biosensors for diagnostics. The development of less expensive, more sensitive and more specific biosensors is indeed necessary both to face contemporary healthcare challenges and to enable the advent of personalized medicine. However, the current fabrication methods present many challenges due among others to the required use of high temperature and compatibility between the optical gain material and the substrate. As a result, new approaches based on micro-structuring of colloidal nanoparticle films are being currently developed (Erdem et al, Nano Lett. 2020, 20, 6459–6465) Here we propose to fabricate micro-lasers from colloidal semiconductor nanocrystals in order to use them in a novel biosensing diagnostics sensor.

Indeed, recently, the LPEM team has developed an original type of sensor based on energy transfer from whispering gallery modes (WGM, optical modes confined inside a spherical micro-cavity) to dye acceptors present at the proximity of the micro-cavity surface [Jana et al, ACS Nano 2021, 15, 1, 1445]. The design was based on fluorescent semiconductor nanocrystals (or quantum dots, QDs) placed within a polymeric colloidal microsphere. Part of the QD emission coupled to WGMs, which were then able to transfer their energy to acceptor dye-loaded nanoparticles present within the optical near-field outside the polymeric microsphere. We have recently demonstrated that this phenomenon can be harnessed to detect specific biomolecular interactions such as DNA hybridization, opening the way to the design of novel biosensors. This approach is particularly interesting: (i) in contrast to other microcavity-based sensing schemes, it is much simpler to operate and more robust; (ii) the energy transfer is much more efficient than standard Förster Resonant Energy Transfer commonly used in diagnostics. This is due in part to the extension of the optical near-field (80-100 nm vs 5-10 nm for FRET) and to the high quality of the optical cavity which enhances the donor-acceptor interaction by several orders of magnitude. The sensitivity of the current sensor is however limited by the low fraction of QD emission coupled to the WGMs. The uncoupled emission is present as a broad spectral envelope background, which is not engaged in energy transfer, and from which the WGM emission signal is not easily

In this project we propose to overcome the limitations described above by developing a new type of sensor based on lasing micro-cavity energy transfer. Here, we need to design a low cost and effective method to build optical micro-cavities with specific sizes and shapes, such as micro-disks or micro-rings. In addition, to reach maximal sensitivities, we need to optimize the optical properties of our semiconductor nanocrystals in order to enable laser operation at ambient temperature and low pump power. To achieve these goals, we will therefore design semiconductor nanocrystals optimized for lasing and develop a new method to manufacture nanocrystal micro-lasers using photolithography, and then develop their surface biofunctionalization.

Compared to the use of polymeric colloidal microspheres used previously, its advantage lies in the deterministic positioning of the microcavities, facilitating optimized detection schemes as will be detailed below. More importantly, the operation above the lasing threshold eliminates the uncoupled background emission and maximizes the efficiency of emission coupling into the optical cavity, thereby considerably increasing the sensor sensitivity.

Methodology

A first step of the project is the synthesis of colloidal semiconductor nanocrystals optimized for their optical gain, in particular to enable low-threshold lasing. These nanocrystals, in particular 0D spherical quantum dots (QDs) and 2D-extended nanoplatelets (NPLs), have been investigated by other groups for their lasing properties. In particular, NPLs, which have been originally developed at LPEM, show exceptionally promising performances. We will first synthesize QDs and NPLs following protocols already developed at LPEM to start the optimization of the micro-fabrication procedures in the next step, then develop novel materials with optimized properties to obtain lower lasing thresholds. In particular, the optimization of the optical laser gain necessitates minimizing reabsorption by nanocrystals and reducing Auger recombination of multiexcitons to enable population inversion and lasing. To achieve this, we will examine novel materials such as type-II NPL heterostructures. The synthesis, structural and optical properties will be characterized at LPEM, in particular regarding their optical gain properties.

A second step consists in the fabrication of the micro-lasers, using patterning of thick and compact microstructures (disks or rings) containing fluorescent nanocrystals at INSP. We will use negative photoresist like SU-8 and dope it with nanocrystals. Doped SU-8 will be deposited as thick compact films onto a glass substrate. The resist will be insulated by a controlled shaped laser under optical microscopy. This will enable cross-linking the resin, trapping nanocrystals inside. The shape of the laser will be engineered by a spatial light modulator in order to fabricate not only disks but also circular rings. The non-irradiated portions of the SU-8 nanocrystal doped film will then be washed away with an appropriate solvent, leaving the microstructures following the irradiation patterns. In a second stage of the project, in order to detect more efficiently light out of the microcavity, we will fabricate dielectric waveguides of controlled width and height and placed at controlled distances from the nanocrystal doped microstructures, using undoped SU-8 as an efficient waveguide material [Beche et al, Opt. Comm, 2004, 230:91] The film will then be irradiated in a controlled pattern at specific distances from the waveguides, using similar laser photolithography technique. The sample will be characterized by electron and optical microscopy.

The emission spectra of the micro-structures will be characterized to optimize the fabrication process, first to maximize the quality factor of the obtained optical microcavities. The optimized structures will then be realized at different distances of the waveguide, to find the proper balance between coupling and preservation of the quality factor of the WGMs. They will then be characterized for lasing using different pulsed excitation sources both at INSP and LPEM.

The final step will consist in introducing specific surface chemical functionalities, to the microstructure. This will enable further conjugation with specific biomolecules. For example, carboxylic acids could be used as chemical function for conjugation by amide formation using a NHS ester intermediate. This functionality could be achieved by introducing a fraction of functional monomers into the SU-8 resin before the photolithography step, or by activating surface epoxy groups by ozone treatment after the lithography. These reactive functions could then be used to graft model biomolecules (such as streptavidin) and test the sensitivity of the device to detect biotinylated dye acceptors as a proof of principle, towards the development of future functional biosensors.

Role of each partner

The LPEM team is specialized in the synthesis of semiconductor nanocrystals and their use in optoelectronic or biosensing applications. It is at the forefront in the development of 2D NPLs and core/shell QDs (Moghaddam et al, JACS, 2021 143:1863; Dufour et al, ACS Nano 2019, 13:5326–5334;) and in surface functionalization for bio-sensing.(Debayle, Biomaterials, 2019; Tasso et al, ACS Nano, 2015, 9:11479–11489). The INSP team is specialized in developing original photo-lithography methods for microfabricating complex structures, coupling QDs with dielectric or metallic micro- and nano-structures, and studying their optical properties.

Positioning

The development of sensors using energy transfer from whispering gallery modes of microcavities is highly innovative. While many groups in the world are developing sensors based on detection of spectral shifts of whispering gallery modes, this new type of sensors has just recently been proposed by the LPEM (Jana et al, ACS Nano 2021, 15:1445–1453). Using specially designed semiconductor QD and nanoplatelets and an easy and versatile strategy to fabricate micro-lasers would bring us one step closer to the realization of robust, ultra-sensitive biosensors.

This project also represents a novel research direction for both LPEM and INSP. In addition to the novelty of the proposed design, this will start a novel collaboration between these two teams. On the LPEM side, the ability to design and fabricate microstructures made from nanocrystal thick films will provide a new field of application for the nanocrystal materials and a new way to manipulate their optical properties. INSP has an expertise in single photon engineering, by coupling nanostructures to nanocrystals. From the INSP side, sensing applications open a new domain in a more applicative perspective.

This multidisciplinary project therefore fits well the Institut des Matériaux, at the interface between physics and chemistry. It lies within several of the Institut main themes: fundamental research, methods, techniques, innovation, with a strong potential for application in healthcare, with the design of innovative diagnostic biosensors.

Candidate profile

The candidate should possess a solid background in physics and optics, with an interest for the synthesis of nanomaterials and for interdisciplinary studies.

**Merci d'enregistrer votre fichier au format PDF et de le nommer :
«ACRONYME de l'initiative/institut – AAP 2021 – NOM Porteur.euse Projet »**

*Fichier envoyer simultanément par e-mail à l'ED de rattachement et au programme :
cd_instituts_et_initiatives@listes.upmc.fr avant le 20 février.*