Building energy efficient quantum dot-based LED through rational optimization

A. Scientific context of the project

Context: The lighting industry plays a pivotal role in the global economy, accounting for approximately 20% of electricity consumption and contributing to 6% of greenhouse gas emissions as of 2013[1]. Without swift adoption of energy-efficient technologies, such as light-emitting diodes (LEDs) and robust policy changes, energy use for lighting is projected to increase by 60% by 2030[2]. **This growth would exacerbate CO_2 emissions linked to energy production, intensifying global warming and contributing to ongoing climate change**.

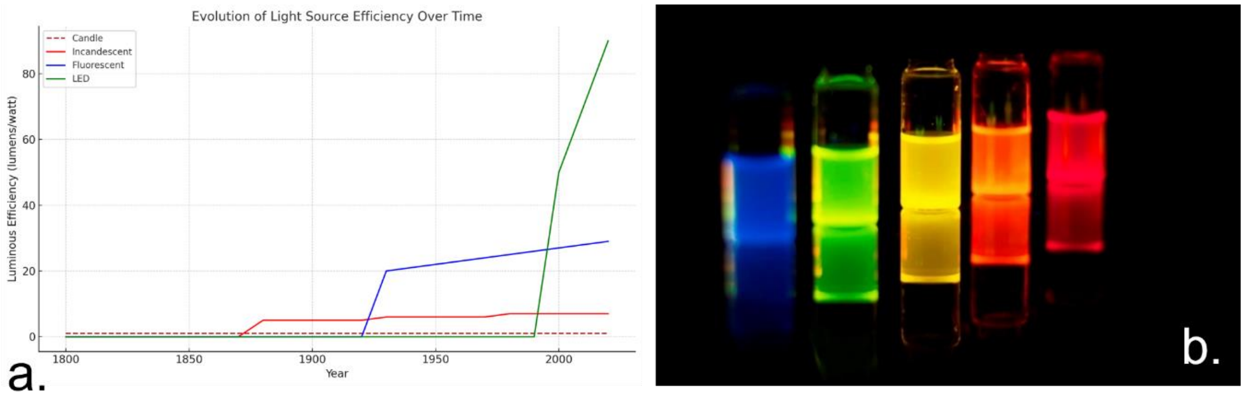

***Figure 1**: Nanocrystals as light source. a. Luminous efficiency of various light emitting technology over the years. AI generated graph. b. Image of a set of colloidal quantum dots with various size as synthetized at ESPCI.*

Despite significant advancements in Lightning technology (Figure 1a), inefficiencies persist, particularly in light extraction, with energy losses reaching as high as 80%[3]. These losses not only diminish the overall performance of lighting devices but also hinder the widespread adoption of more sustainable and energy-efficient solutions. **Enhancing LED efficiency, therefore, is both a pressing technological challenge and an economic necessity**[4].

Colloidal Quantum dots (CQDs) are in solution grown nanoparticles whose emission color can be finely tuned by their size, see Figure 1b. The pioneering work from the late 80's early 90's of Ekimov, Brus, and Bawendi[5], who were awarded the 2023 Nobel Prize in Chemistry, laid the foundation for this field[6,7]. Up to 2000's, nanocrystal have been investigated using optical method down to the single particle level. One of the key advantages of CQDs is their narrow emission bandwidth which give them an advantage compared to fluorophore such as Ce:YAG massively used up to now in lighting applications. The development of colloidal heterostructures, essential for achieving high-efficiency CQDs, has further enabled their adoption in display technologies.

Significant efforts have been made to transition to electrically driven CQD-based devices, leading to the development of quantum-dot light-emitting diodes (QLEDs). Achieving this milestone required overcoming the central challenge of enabling charge conduction in CQD arrays. The Bulović's group at MIT played a pioneering role by reporting the first QLEDs,[8] a development that was subsequently advanced by other researchers, including Peng[9], Samsung, and more recently Klimov, whose work extended to pushing the boundaries of QLEDs towards laser diodes[10]. These advancements have positioned QLEDs as competitive alternatives in the visible light spectrum, particularly for commercial applications such as consumer electronics and energy-efficient lighting systems. **Despite these achievements, key challenges remain to further enhance the rationality of the design of such stack.** Current main concept for the design of quantum-dots based LED relies on the measurement of band alignment of each layer independently and then “hope” that the pristine properties remain mostly the same as device operate. This clearly neglects the change in dielectric environment and the coupling between layers in the LED stack, despite the latter being significant due to the large current flowing in the system. **Therefore, methods compatible with *in-situ* and *operando* measurements become of utmost importance**. At INSP this strategy has been growing for the last two years and the arrival of the project PI. However, current measurements are based on planar device geometry (transistor, photoconductor) and remain incompatible with diode stack that require *in-depth* analysis. This is why the group just get equipped of the first setup in region Ile de France dedicated on hard X ray photoemission (Phi Genesis) to specifically address this type of question.

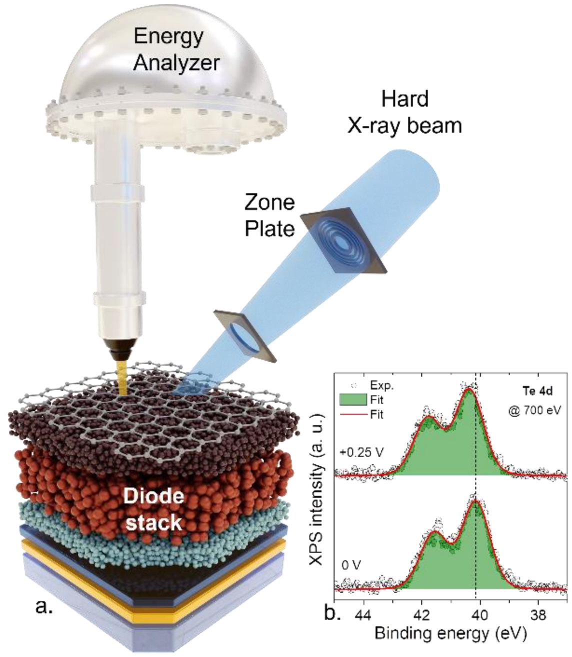

Figure 2 : *a. Image of a CQD-based LED stack probed via operando X-ray photoemission. b. Preliminary results obtained for a diode stack made of HgTe CQDs, showing a shift of the core level peak under bias application*

Scientific approach: our project aims to grow CQDs (at ESPCI) that are relevant for LEDs, specifically CdSe/ZnS core- shell materials, possibly with graded shell to limit Auger recombination[11,12]. The shell thickness will be optimized to achieve both bright luminescence and compatible with charge injection.

At INSP, in the clean room and glove box setup, the material will be integrated into a diode stack. **Unlike conventional stack, it will be updated to have a top contact of graphene (Gr)** (Figure 2a). The diode architecture will be glass/ITO/PEDOT/PVK/polyTPD/CQDs/ZnO/Gr[13,14]. Graphene offers the benefit of being transparent to light and electrons, thus enabling *operando* photoemission. We have obtained a preliminary result demonstrating the feasibility of such measurements for an infrared detector where we observed a bias induced shift of a core level relative to the optically active material (Figure 2b). While this preliminary result was obtained at synchrotron SOLEIL, we now aim to conduct the same measurements on our INSP setup, with complementary measurements will also be conducted at the synchrotron facilities. The goal is to reconstruct the full potential profile along the diode stack, which will enable the optimization of its operation and the reduction of the LED driving bias.

Risks and mitigation: The risk associated with the not tunable photon energy (*i.e.,* only Al Kα = 1486.6 eV and Cr Kα = 5414.7 eV) is that it will provide only a partial exploration of the *in-depth* energy landscape, limiting our ability to determine where bias is applied in the stack. This limitation arises from the inelastic mean free path (IMFP) of the photoelectrons, which restricts the accessible depth range. With our current setup, photon energies up to 5414.7 ev can be used, limiting the probing depth to approximately 30 nm. This constraint can be mitigated by using synchrotron radiation setups, which extend photon energies up to 12 keV, thereby increasing the depth range to approximately 50 nm. Additionally, advanced data analysis methods, such as inelastic background modeling, enable access to information from buried interfaces up to 200 nm[15]. Then, to complete the data set, additional measurements will be conducted at synchrotron facilities after securing the device operation.

Another risk is that LED performance may be limited by light extraction rather than bias distribution. To address this, a metasurface, such as a metallic grating, will be added to assist coupling to the far field.

Adequacy to the call: The project is focused on building more efficient LEDs, aiming to push their external quantum efficiency into the high 20 % range. Such value corresponds to an internal efficiency close to 1 (one photon emitted per injected electron-hole pair). **This aligns well with the selected topic of the year, which emphasizes the development of innovative materials that contribute to a greener society by reducing energy consumption and mitigating the environmental impact of lighting**.

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B. Skills and coherence of team

The consortium will consist of two teams, with **Debora Pierucci** from INSP leading the device and photoemission side, and **Sandrine Ithurria** from LPEM (ESPCI, SU) responsible for CDQs growth. Both teams have a history of collaboration (>70 joint publications) and have developed complementary expertise in material characterization. The consortium has full control of the process, from the growth of active materials and device design to the unique *operando* setup. A possible candidate for the PhD project has been identified (Giorgia Strobbia, Master II internship student at INSP), however, the hiring process will remain open and will follow the iMAT procedure, including a public call.

C. Research plan with provisional calendar

During the beginning of the PhD (first few months) the applicant will undergo training in clean room fabrication, LED characterization and will also learn about photoemission measurements.

Then, after a six months period in which the applicant will have gained autonomy in LED design, the applicant will also learn how to grow CQDs to facilitate constructive discussions with the sample provider. At ESPCI, the applicant will further conduct luminescence characterization (PL spectrum and time resolved measurements). In a second step, we intend to focus on upgrading the LED stack by replacing the top electrode with graphene to make it compatible with *operando* XPS measurements. This will involve a 3 months training period (towards the end of the first year) focused on graphene deposition, followed by optimization to ensure compatibility with the CQD stack. A series of measurements will be conducted on the laboratory platform to confirm that measurements can be performed while preserving the normal operation of the device. Meanwhile proposals will be submitted to obtain beamtimes at synchrotron facilities (e.g., Galaxie beamline at SOLEIL or I09 at Diamond (UK)).

Following the beamtimes (first part of second year) we intend to develop a code to reconstruct the vertical electric field distribution from data set acquired at various bias and photon energies. In the second part of second year, the focus will be on proposing an optimized diode stack, where the built-in electric field spatially overlaps better with the CQDs layer, aiming to demonstrate a reduced driving voltage. The goal is to obtain a consistent dataset from the *operando* probed electric field profile obtained by photoemission and correlate it with the device performances.

In the third year, efforts will focus on promoting these results toward various scientific communities (*e.g.*, those focused on CQDs at conference such as GRC, MRS, NanoGe and those of photoemission at event such as JNSPE, ECASIA). A key objective will be to have 2-3 publications published before starting the PhD writing which will ease the process.