DROP-IT

DELIVERABLE 4.3

Inkjet-printed RGB LED arrays based on BLFPs

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1 Introduction

Fabrication of a small matrix (10x10 pixels) with RGB-subpixels as a raw display whose pixels emit white light LED. These arrays will be based on B-LFPs by inkjet printing, as optimized in this work package for single-color LEDs.

1.1 Purpose of the report

From D 4.1 we obtained the most suitable LED device structures and architectures, where the validated transport layers are tested with the selected promising red emitting G-LFP. In the same deliverable several inkjet-printed B-LFP thin films ($FASnBr_3$, $MASnBr_3$, $MAFASnBr_3$, $MASnI_3$) were tested, as benchmark in terms of efficiency and stability, but none of them showed in terms of PL emission, values below 1%, promising devices after inkjet printing the thin active layers. Consequently the main efforts in this work are focused on the analysis of current literature for the implementation of arrays of RGB LEDs based on G-LFP. Different approaches are presented to face the difficulties of displays manufacturing and to achieve with the inkjet technology the standard resolution for display geometry.

Displays can be divided mainly into two categories, those with self-emissive pixels like OLEDs and MicroLED and those in which pixels are passive (LCD) and require backlighting. Those displays with self-emissive pixel provide a much rich visual experience due to the infinite depth of contrast, the capacity to deliver higher luminance, faster response times, better energy efficiency and the tighter control over the information delivered to each subpixel. OLED technology is mature and well introduced into the market although it is well known that this organic technology degrades fast, especially the blue OLED subpixels. MicroLED technology is based on self-emissive inorganic InGaN LEDs (also used for lighting) which rival and surpasses OLED in performance and do not degrade. Nevertheless, InGaN microLEDs are produced using conventional microchip technology which is based on high cost III-V materials, which are fabricated with complex technologies in clean rooms and require advanced lithography. Additionally, MicroLED displays are assembled from many of those chips which are placed together and require a complex and expensive built in procedure.
On the other hand, patterning of different emissive materials is a key element in the manufacturing of OLED displays. Vacuum evaporation of small emissive molecules is the prevalent technology to deposit the electroluminescent layers. In combination with masks, this evaporation method is used to manufacture small and medium size displays.

Consequently, there still not up to now any established technology that can compete with OLEDs and which is based on inorganic emissive materials for LEDs that do not degrade with time and that do not require complex and expensive material and/or device production.

Nevertheless, the are some emerging inorganic (or hybrid inorganic-organic) technologies suitable to achieve this goal, like ones are based on solution processed Lead Free Perovskite (LFP) materials. Solution processable methods have been used recently to produce large-area and low-cost optoelectronic devices and solar cells based on LFPs.

In the past deliverables several approaches for the formulation of suitable inks for inkjet printing based on LFP were explored to obtain the best combinations of inks stability and optimal printability, which in turn improve the printed layer performance due to the good wettability of the inks. Furthermore, we had presented different printing strategies and procedures by adjusting patters, velocity, temperature, and post-processing of the layers to optimize the quality of the layers and the light emission. Once the inks and the printing procedure have been optimized, we find that the post-deposition treatment is relevant to achieve the best uniformity and best properties. Annealing and sintering in vacuum in an oven produce high quality layers.

In order to promote the best performance when manufacturing perovskite LEDs we should contemplate the following:

- Non-radiative recombination losses must be minimized which means maximizing the PLQY. We observed in the last works, D4.1, the use of 2D perovskite is a novel promising alternative.
- The printed perovskite active layer must present a reliable and replicable morphology to guarantee smooth, homogeneous, and pinhole-free films which are key characteristics to reduce charge recombination at the interfaces.
- The development and selection of most appropriate HTLs and ETLs compatibles with the energy levels of new LFP materials which differ sensibly from traditional organic semiconductors.

When all these requirements are met, PeLEDs with competitive EQE comparable to the OLED can be reached.

2 Description of work in literature

2.1 Inkjet printing

Considering all these preconditions, in order to inkjet print PeLED displays, it is necessary to achieve a high specification of both drop placement and drop volume. A single misplaced or outsized drop might produce an imperceptible defect in a graphics print, but the same error in a display might cause a pixel to short-circuit and fail completely, or emit at a different brightness, and hence result in a much more visible defect.
Once the ink lands on the substrate, the wet droplets must dry by the removal of the solvents used to carry the active material without the benefit of absorption into the substrate; the solute initially distributed uniformly in the hemispherical wet drop must dry to a flat film. Also, the solvents and other additives in the ink must evaporate properly to promote the best crystal growth and smoothness avoiding without affecting the performance of the resulting device.

In resume the complete PeLED fabrication for displays implies the development of current inkjet printing technology to new inert and versatile conditions like glovebox (to avoid degradation of printed layers), novel printheads that can accomplish low controlled drop volumes ejection, ink formulation continuously changing and adapting, substrate evolution and related surface processes which facilitate the printing step and post-process annealing methods.

By the precise deposition of droplets using the drop-on-demand inkjet printing technique, thin red- (R), green- (G), blue- (B), and/or white-emitting material layer (EML) pixels were fabricated for high performance light-emitting pixel arrays of organic LEDs (OLEDs) as well as QD LEDs (QD-LEDs).[refs]

2.2 Standard Display Geometry

LED displays are arrays of pixels made up of red, green and blue sub-pixels, with a typical geometry as shown in Figure … . The number of pixels and their size are determined by the application. In general, for high-definition televisions the pixel array is 1080 × 1920 and typical sizes range from 37 to 65 in. (940–1651 mm) on the diagonal, corresponding to sub-pixel pitches of 142 and 250 µm respectively. For handheld devices such as smartphones, the pixel arrays are up to a wide video graphics array or 480×800 pixels with sizes ranging from 2.9 to 3.8 in. (74–97 mm) diagonal corresponding to sub-pixel pitches of 26 and 35 μm respectively.

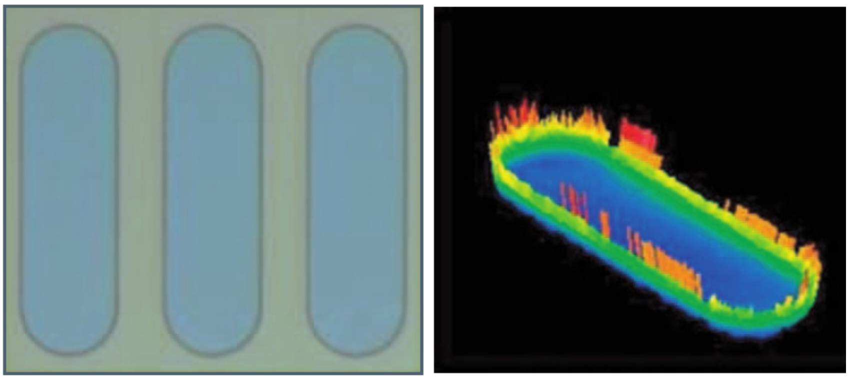

Figure 1: Photomicrograph of printed PEDOT and white light interferometry representation of a PEDOT film profile in one of the wells– the uniformly coloured areas represent a thickness variation of ±2 nm (See plate section for coloured version).

It is demonstrated, considering the main two sizes of pixels (small pixel 30 μm common in smartphone display and big one 180 μm standard in a large TV display) that for a well dimension L, the ink volume required to attain a certain fixed depth scales with L2, whereas the ink contained in the well scales as L3. It follows that ideally, with everything else being equal, the solid content should scale as 1/L.

In inkjet printing, different pixels are printed with different nozzles, and differences in volume from nozzle to nozzle will give rise to different thickness of the emissive layer, resulting in a different brightness from adjacent pixels. Nowadays this possible weakness is solved by the printer software which integrated system allow design the waveform to the selected printhead for each functional ink adjusting/compensating minutely the drop volume on a nozzle-by-nozzle scale.

The solid content is typically between 0.2 and 2.5% w/v. Considering the displays technology constraints, the selected inkjet printing technology should ensure the same solid content for different pixel volumes to be filled up and at the same time the required amount of ink can be contained by the well for small pixels

To prevent overspill of ink from one pixel to the neighbouring one, prior to the inkjet printing deposition step, the substrates were usually prepatterned with insulating polymeric walls of acrylate or polyimide materials surrounding each pixel site in the form of a bank-like structure, into which the ink droplets can be held.

The balance between wetting and containment is also adjusted through the careful control of the surface energies of the pixel and bank surfaces. Such surface energy control is achieved through selection of the material used for the bank structures, substrate-processing methods and surface treatments before printing such as plasma, UV-ozone or solution treatment.

The polymer walls are hydrophobic while the substrate is hydrophilic, so when a drop of hydrophilic ink reaches the well, it wets the substrate. If the printhead and the substrate are slightly misaligned or the droplets deviate during flying, these can touch the polymer wall and de-wet eventually falling inside the well confining the emissive material. As a result, electroluminescent pixels with position and size accuracy within few micrometres can be processed. High resolutions exceeding 200 pixels per inch, that are suitable for large size but also for medium and small size displays can be created using this approach.

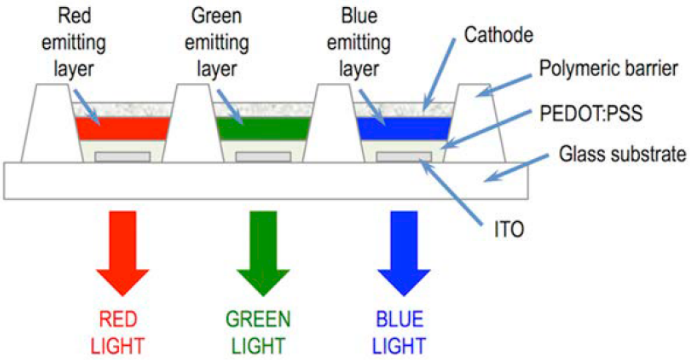

Figure 2: Schematic pixel structure of a red, green and blue (RGB) organic light emitting diodes (OLED) display. Materials **2016**, 9, 910

As example, the work presented lately by…. [J Soc Inf Display. 2022;1–10] achieved Inkjet-printed multi-color arrays based on eco-friendly quantum dot light emitting diodes using inkjet printing technology onto pre-fabricated bank arrays by a conventional photolithography, Figure 3.

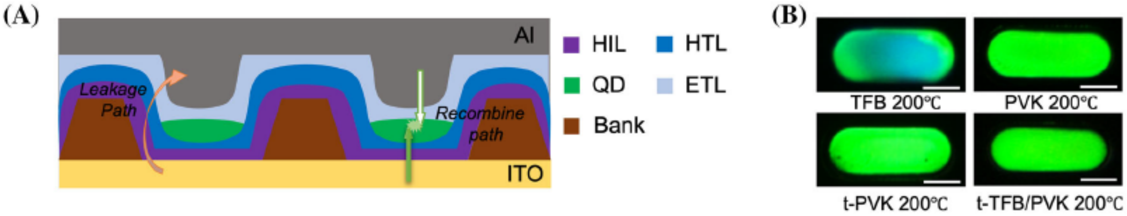

Figure 3: Inkjet-printed QLED with band structure. (A) Schematic illustration of inkjet-printed QLEDs with bank structures. (B) The EL images of green InP-based QLED pixels with different HTLs. Performance of QLEDs with different HTLs, including

Recently, also the company Samsung Display *[J Soc Inf Display. 2022;30:433–440]* presented the all-inkjet printed QD-LED devices which were successfully fabricated, demonstrating Inkjet printing is believed to be the most feasible tool of patterning full color QD-LED display for mass production.

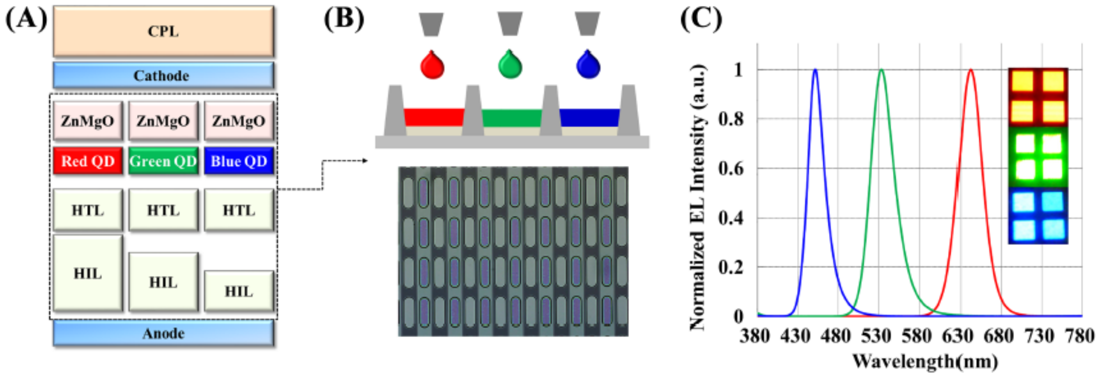

Figure 7: (A) Device structure of all inkjet-printed RGB QD-LED subpixels. (B) Schematic diagram of inkjet printing process and pixel layout with subpixel size of 120 µm _ 40 µm. (C) Normalized EL spectra and photos (inset) of RGB QD-LED devices measured at 5 V. *[J Soc Inf Display. 2022;30:433–440. DOI: 10.1002/jsid.1126]*

Alternatively to the above-mentioned technique, Small Sci. 2022, 2200017 presents an innovative work where the pre-patterning process is avoided because generally requires complex photolithographic procedures and at the same time has the potential to contaminate the surface of the substrate, unavoidably deteriorating device performance capabilities.

The new strategy proposed take the advantage of using inkjet printing as a subtractive tool capable of site selectively removing small areas of pre-deposited layers, that is, inkjet etching. Specifically, a solvent in the droplet locally dissolves a pre-deposited polymer layer, resulting in a mechanism of via-hole formation thanks to the commonly known coffee-ring effect due to the microfluid flows in a sessile droplet ejection. Such an inkjet-based selective etching process has several advantages over conventional complex photolithographic etching processes.

Figure 4 shows an example of inkjet-printed micro-OLEDs (µ-OLEDs) which were produced by the subsequent inkjet printing of light-emitting materials into the inkjet-etched open via-holes.

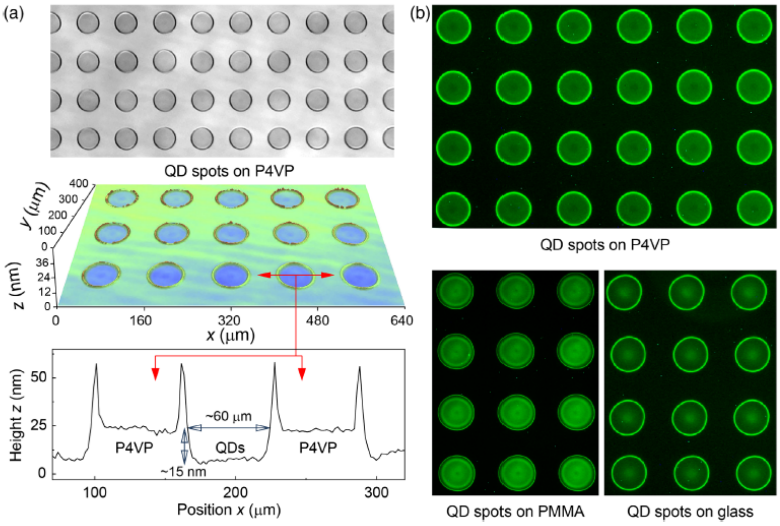

Figure 4: a) Optical microscopy image (upper), 3D surface image (middle), and 2D profile (lower) of a rectangular spot array of single-inkjet-printed Zn–Cu–In–S/ZnS (ZCIS/ZnS) core/shell QDs at 200 dpi on stacked layers of PVK/P4VP (50/30 nm) with an orifice diameter of 50 µm. Self-organized circular inkjet-inlaid spots are shown in the surface profile images. Each droplet forms a circular microspot pixel with a diameter of _60 µm. b) Fluorescence microscopy images of rectangular spot arrays of inkjet-printed ZCIS/ZnS QDs on stacked layers of PVK/P4VP (upper), on a comparative 30 nm-thick PMMA layer (lower left), and on a bare glass substrate (lower right). (Small Sci. **2022**, 2200017)

To easily implement the proposed inkjet-printing processes, a functional layer that plays multiple roles can be introduced in the inkjet-printing process, as presented in Figure 5.

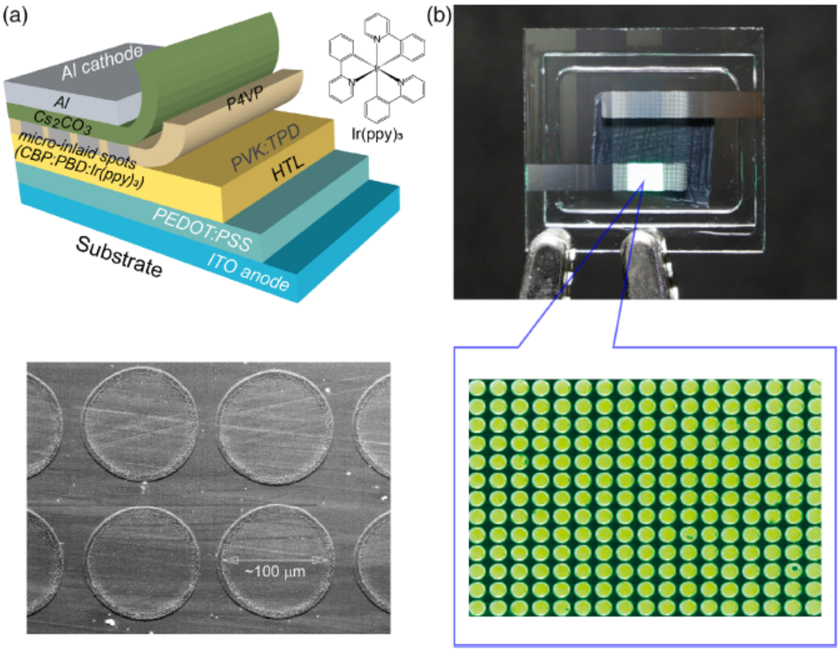

Figure 5: a) Schematic illustration of µ-OLED pixels with inkjet-inlaid EML spots of CBP:PBD:Ir(ppy)3 in an insulating P4VP layer (upper) and SEM image of inkjet-inlaid EML spots in a P4VP layer (lower). b) Photograph of a green-emitting µ-OLED pixel array (upper, active area: 3mm_ 2 mm) and a microscopy image of the light-emitting pixels (lower) at an applied voltage of 5.0 V. Microinlaid EML spots were fabricated with a resolution of _180 dpi (Small Sci. **2022**, 2200017).

2.3 Strategies of high-resolution pixel arrays

Among several key requirements for inkjet printing PeLED displays, special attention must be paid to drop position (controlling the surface properties of the substrate) and minimizing the feature size of the droplets generated to increase the pixel resolution guaranteeing expected print reliability and throughput.

The specification for drop position is determined by the geometry of the display to be printed, the drop size dispensed by the head and the surface energies of ink and surfaces.

As an example, displays with a color pixel pitch of between 100 and 150 ppi (corresponding to sub-pixel dimensions of ~85–55 µm) printed with a 10 pl cartridge (corresponding to a drop diameter of ~55 µm) on suitable treated surfaces require drop-landing accuracies of better than ±10 µm.

Print-heads are available that are specifically designed for printed electronics applications, or suitable for them, with drop deviations of less than 10 mrad. For a typical head–substrate distance, this would give rise to drop position errors of less than ±5 µm, the case of the selected Dimatix printer.

For example, in the Dimatix D-128 inkjet-printed system, when the nozzle diameter is reduced from 21 to 9 mm, the volume of the standard ejected droplet decreases from 10 to 1 pL.

In addition to the geometrical parameters, handling/tuning the substrate wettability the surface properties ensure the reliability and feasibility of resultant deposited pattern size.

In contrast to the above treatment, Frisbie et al. [] developed a substrate with microchannels, treated by physical or chemical methods, with a well-designed pattern named "pixel-pit" which forces inks, driven by capillary forces, to deposit precisely without any spontaneous spreading.

Similarly, Sung et al. [] combined inkjet printing with transfer printing to create an innovative liquid-bridge-mediated transfer technique. The ejected ink was favorably transferred to the specified location with a nanoscale feature size.

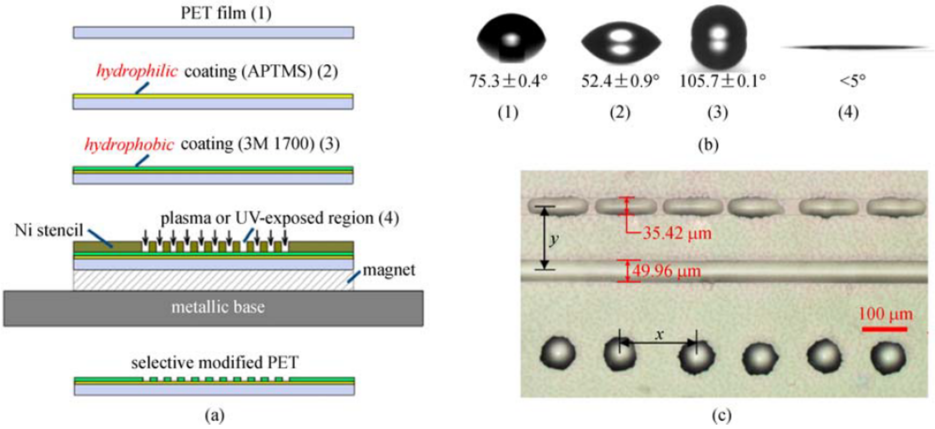

Figure 6: (a) Preparation of patterning PET film by wetting and dewetting treatment. (b) WCA on various post-treatment PET surfaces: (1) untreated PET film, (2) treated by hydrophilic APTMS, (3) treated by hydrophobic 3M Novec 1700, (4) selectively hydrophilic treatment by either O2/Ar plasma or UV/O3. (c) IJP test on type b-4 PET film. [Fresbie et al.]

3 Deviations from the workplan

In this report, we propose the possible architecture for the LED array fabrication without any trial. We consider that within D4.1 we demonstrated the capability of obtaining stable and efficient red emitting devices based on G-LFP (2D tin-based phases), but still no green and blue components due to the impossibility to obtain inkjet-printed layers with B-LFPs ($ASnBr_3$ perovskites) with sufficient quality. In the next week we will propose implementing the printing array with a single color meanwhile the other colors will be properly obtained in the measure we advance with the proposed G-LFP materials emitting green and blue colors.

4 Conclusions & Future directions

In this report, we have presented the feasibility, in current literature, of using the inkjet printing approach to deposit QDs in a predefined pixel pattern with several formats. The successful operation of the RGB printed devices indicates the potential of the inkjet printing approach in the fabrication of full-color QDLEDs for display application. However, further optimization of print quality is still needed in order to eliminate the formation of pinholes, thus maximizing energy transfer from organic layers to the QDs and in turn increasing the performance of the devices.

From the full analysis of the literature, Inkjet printing is believed to be the most feasible tool of patterning full color QD-LED display for mass production, because QD-LED and CTL (charge transport layer) are solution-state materials and the inkjet printing technology including inkjet printers and ink materials are pretty matured.