## **Supplementary Information**

Air stable eco-friendly quantum dots with light-mediated photoinitiator for inkjet printed flexible light emitting diode

Hanleem Lee, Yo-Han Suh, Xiangbing Fan, Limeng Ni, Jiajie Yang, Yoonwoo Kim, Jeong-Wan Jo, Hyung Woo Choi, Sung-min Jung, Dong-Wook Shin\*, Sanghyo Lee\*, and Jong Min Kim

Department of Electrical Engineering, University of Cambridge, 9 JJ Thomson Avenue, CB3 0FA, United Kingdom

E-mail: ds887@cam.ac.uk, sl920@cam.ac.uk

This PDF file includes:

## **Table of Contents**

I.	Material Characterization	S1 - S4
II.	Ink Characterization	S5-S10
III.	Device Preparation and Their Characterization	S11 - S18

#### I. Material characterization

#### Synthesis of quantum dot

<u>*Materials:*</u> Indium chloride (InCl<sub>3</sub>, 99.999 %), zinc acetate (Zn(Acet)<sub>2</sub>, 99.99%), oleic acid (OA, 90 %, technical grade), 1-Octadecene (ODE, 90 %, technical grade), tris(trimethylsilyl)phosphine (TMSP, 95 %), sulfur (S, 99.99 %), selenium (Se, 99.99 %), trioctylphosphine (TOP, 97 %), 1-dodecanethiol (1-DDT, 98 %), and octane (95 %) were purchased from Sigma-Aldrich. Chloroform (HPLC grade), acetonitrile (HPLC grade), and acetone (HPCL grade) were purchased from Fisher scientific. Type S, CYTOP was purchased from AGC chemical. All chemicals were used without further purification.

<u>Preparation of pristine InP core</u>: Initially, a zinc oleate precursor was prepared: 15 mmol of  $Zn(Acet)_2$  and 30 mmol of OA mixed at room temperature, degassing at 120 °C under the vacuum for over 3 hours to remove acetic acid in the mixture. After then, ODE was added into the zinc oleate precursor to make 0.5 M concentration of a solution. 0.1 mmol of indium precursor (0.5M, InCl<sub>3</sub> in TOP solution) was mixed with 2 mmol zinc oleate precursor at room temperature, and then a mixture was heated at 280 °C in N<sub>2</sub> environment. 0.1 mmol of TMSP/TOP (10 wt%) was rapidly injected into the hot solution. The InP core was synthezied at 280 °C for 1 h. The InP core was precipitated and purified with chloroform and acetone.

<u>Preparation InP@ESC core</u>: Initially, a zinc oleate precursor was prepared: 15 mmol of Zn(Acet)<sub>2</sub> and 30 mmol of OA mixed at room temperature, degassing at 120 °C under the vacuum for over 3 hours to remove acetic acid in the mixture. After then, ODE was added into the zinc oleate precursor to make a 0.5 M concentration of solution. 0.1 mmol of indium precursor (0.5M, InCl<sub>3</sub> in TOP solution), and 0.3 mmol of 1-DDT or TOP/S (0.5 M) were mixed with 2 mmol zinc oleate precursor at room temperature, and then a mixture was heated at 280 °C in N<sub>2</sub> environment. 0.1 mmol of TMSP/TOP (10 wt%) was rapidly injected into the hot solution. The InP core was synthezied at 280 °C for 1 h. The InP core was precipitated and purified with chloroform and acetone.

<u>Preparation of InP@ZnS QD (Blue)</u>: 4 ml of ODE was injected into the InP@ESC core QDs solution to quench temperature to 150 °C. 0.9 mmol of S/TOP (1 M) was injected into InP QD solution at 150 °C in N<sub>2</sub> environment. After then, the temperature was increased to 300 °C and maintained for 1 h. The InP@ZnS QD was precipitated and purified with chloroform and acetone.

<u>Preparation of InP@ZnSeS QD (Green)</u>: 4 ml of ODE was injected into the pristine InP core QDs solution to quench temperature to 150 °C. 0.4 mmol of S/TOP (1 M) and 0.5 mmol of Se/TOP (1 M) were injected into InP QD solution at 150 °C in  $N_2$  environment. After then, the temperature was increased to 300 °C and maintained for 1 h. The InP@ZnSeS QD was precipitated and purified with chloroform and acetone.

<u>Preparation of In-Zn-P complex for core growth:</u> 1 mmol of indium acetate, 1.5 mmol of zinc acetate, 4 mmol of oleic acid, and 10 mL of 1-octadecane were stirred at 140 °C for 3 hours under vacuum condition to remove acetic acid. The colour of the solution became transparent as the temperature was increased. After 3 hours, the 0.066 mmol of tris(trimethylsilyl) phosphine and 1 mL of trioctylphosphine were mixed at room temperature for 1 hour. The solution colour varied from transparent to pale-yellow colour.

<u>Preparation of InP@ZnSeS QD (Red)</u>: 4 ml of ODE was injected into the pristine InP core QDs solution. 5 mL of In-Zn-P solution was slowly injected at 280 °C (Injection late: 1mL/h) to form larger nuclei. 0.4 mmol of S/TOP (1 M) and 0.5 mmol of Se/TOP (1 M) were injected into InP QD solution at 150 °C in N<sub>2</sub> environment. After then, the temperature was increased to 300 °C and maintained for 1 h. The InP@ZnSeS QD was precipitated and purified with chloroform and acetone.

<u>Preparation of ZnMgO (5% Mg doping)</u>: Initially, the zinc and magnesium solution was prepared: 0.285 mmol of Zn(acet)<sub>2</sub> 2H<sub>2</sub>O, 0.015 mmol of Mg(acet)<sub>2</sub> 4H<sub>2</sub>O, and 30 mL of DMSO mixed at room temperature. After then, 5 mmol of TMAH/EtOH (0.5M) solution was slowly injected into the zinc and magnesium solution. The ZnMgO NPs was synthesized at room temperature for 1h stirring. The ZnMgO NPs was precipitated and purified with acetone and 1-butanol.



**Figure S1** (a) Schematic illustrations of the hydrodynamic behavior of a droplet of nonvolatile solvent. (bc) Dynamic contact angle at 30 us after drop for  $InP@ZnSe_{0.6}S_{0.4}$  QD ink in hexane/octane with (b) and without PI (c) on HTL.



**Figure S2** (a) Photoluminescence of red, green, blue  $InP@ZnSe_{1-x}S_x$  QD. (b) X-ray diffraction (XRD) spectra of InP-core,  $InP@ZnSe_{0.6}S_{0.4}$ , and InP@ZnS.



Figure S3 Transmission electron microscope image of (a) blue InP@ZnS, (b) green  $InP@ZnSe_{0.6}S_{0.4}$ , and (c) red  $InP@ZnSe_{0.6}S_{0.4}$ .



**Figure S4** The PL spectra of (a) pristine QD, (b) QD/PI before UV irradiation, and (c) QD/PI after UV irradiation with the duration of exposure time in the ambient condition. (d) The water contact angle of QD/PI before UV irradiation and QD/PI after UV irradiation.

#### II. Ink Characterization

<u>Optical absorption spectroscopy</u>: The first excitonic peak position of each QDs ink is measured using the NIR-UV-Vis spectrometer (Agilent Cary 7000 UMS).

<u>Surface Tension</u>: The surface tension of each ink is measured using the pendant drop method (First Ten Angstroms FTA1000B) where drop shape analysis is used to calculate the surface tension from the shadow image of a pendant drop.

<u>Rheometry</u>: A parallel plate rotational rheometer (DHR rheometer TA instruments) is used to calculate the infinite-rate viscosity of each ink.

<u>*Transmission Electron Microscopy:*</u> Transmission electron microscopy (FEI Tecnai F20 FEG TEM) is used to define particle size and shape of the red, green, and blue color QDs.

*Ink Formulation:* Previous studies have demonstrated the controllability of organic and polymer functional inks. For example, a fully inkjet-printed organic LED has performed similarly to a device made by spin coating (Luminous efficacy around 68.2 cd/A with good reliability and high EQE approximately 18.7%).[1] The high reliability and controllability of organic and polymer materials for inkjet printing are related to the process of pattern solidification that occurs post-deposition. The pattern morphology is therefore strongly influenced by the interaction with the substrate and other drops.[2] Organic and polymer materials demonstrate strong van der Waals interactions as the dominant intermolecular interaction during printing, unlike the strong ionic or polar interactions of inorganic materials. Therefore, manipulating the droplet interfacial tension and viscosity using a high boiling point solvent can aid the development of organic and polymer inks as viscosity scaling during post-annealing processing does not greatly affect solute aggregation.[3,4]



**Figure S5** (a-c) Surface tension measurement with various  $InP@ZnSe_{0.6}S_{0.4}$  QD ink with different solvent system: Final ink, which is  $InP@ZnSe_{0.6}S_{0.4}$  QD solution in hexane/octane with photoinitiator (a),  $InP@ZnSe_{0.6}S_{0.4}$  QD in octane (b),  $InP@ZnSe_{0.6}S_{0.4}$  QD in hexane (c). (d) Dynamic contact angle at 30 us after drop for  $InP@ZnSe_{0.6}S_{0.4}$  QD ink in hexane, octane, and hexane/octane (9:1).



**Figure S6** (a-c) Optical image of InP@ZnSe<sub>0.6</sub>S<sub>0.4</sub> line pattern with octane/hexane (1:9) solvent (a), octane (b), and hexane (c). (d-e) Optical image of InP@ZnSe<sub>0.6</sub>S<sub>0.4</sub> line pattern with octane/hexane (1:9) solvent with 40 °C platen temperature.



**Figure S7** (a) Viscosity versus shear rate of ink with and without photoinitiator. Inset: the PL image of spin coated film with and without photoinitiator in ambient condition. (b-d) Dynamic contact angle with final ink as time goes by: (b) 0 us, (c) 10 us, (d) 30 us.



Figure S8 AFM image of printed InP QD layer pattern before UV exposure; (a) the sample is prepared without any drying process, (b) the sample after drying in vacuum.



**Figure S9**. Luminance properties of QD films with green and blue QDs with/without PI as a function of UV exposure time. The films were coated at 2000 rpm for 30 s on 10 X 10 mm glass substrate. The power of UV lamp is 48W.



**Figure S10** Microscopy PL image of printed InP pattern without PI (a) and associated PL intensity profile (b). (c) PL intensity profile of printed InP pattern with PI.



**Figure S11** PL image of printed InP pattern with (a) 150  $\mu$ m x 3 cm with 100  $\mu$ m spacing with different printing cycles, (b) 100  $\mu$ m x 200  $\mu$ m square, and (c) 30  $\mu$ m dot.

#### III. Device Preparation and Their Characterization

InP LED on glass: All solution-processed QLED is fabricated on pixelated ITO coated glass (from Ossila). The conductivity of the anode is around ~20  $\Omega$ /sq. PEDOT: PSS (AI 4083) is spin-coated on the substrate after 60s O<sub>2</sub> plasma treatment as a hole injection layer (HIL). The substrate is baked at 150 °C for 30 min in air. After then, PVK and TFB (from Sigma Aldrich) of 8 mg/ml concentration (1:3 wt%) in chlorobenzene is spin-coated at 2000 rpm for 30 s, followed by baking at 150 °C for 30 min. The synthesized QDs and ZnMgO nanoparticles are either spin-coated or inkjet-printed for the desired purpose.

Spin coating condition - InP@ZnSeS QD (15mg/ml) in octane is spin-coated at 2000 rpm for 30 s and baked at 80 °C for 30 min. After then, ZnMgO nanoparticle in isopropanol is coated at 2000 rpm for 30 s and baked at 80 °C for 30 min. Finally, Al (150 nm) is deposited on the top of ZnMgO layer as a cathode electrode in a high-vacuum chamber (base pressure of ~  $1.5 \times 10^{-7}$  torr) by using E-beam evaporation.

Inkjet printing condition - InP@ZnSeS QD (15mg/ml) in hexane/octane (19:1 vol%) is used for green QD and 23 um drop spacing is used for printing. Blue and Red QD (12 mg/ml) in hexane/octane (19:1 vol%) is used and 40 um drop spacing and 25 um drop spacing is used for best condition. The sample is cured by 365nm UV (4W) for 5 min and baked at 80 °C for 30 min to remove any solvent residue. The ZnMgO nanoparticle with 25mg/ml in isopropanol is also printed. The 30 um drop spacing with 2 printing cycle demonstrates approximately 50 nm thickness.

<u>InP LED on PEN</u>: The flexible QLEDs is fabricated as same as the structure of QLEDs on glass. Initially, ITO on PEN substrate (from Sigma Aldrich) is patterned using a conventional photolithography method to separate the area for anode and cathode electrodes. Each layer such as PEDOT:PSS and PVK/TFB are spin-coated with the same condition that we used for QLEDs on glass and baked at 130 °C for 1 hour to prevent plastic deformation of ITO/PEN substrate. The further procedures (i.e. coating of QDs, ZnMgO, Al deposition) are the same for that of glass.

For all solution process QLEDs, PEDOT:PSS electrode (PH 1000) is fabricated by spin coating. PH 1000 is mixed with the DMSO at 9:1 volume ratio and 50ul ethylene glycol in 10 ml PEDOT:PSS solution is added to increase the conductivity of PEDOT:PSS electrode. After 10min sonication, PEDOT:PSS is spin-coated 3 times at 2500 rpm for 30 s on PEN substrate. The other procedure is the same for that of QLEDs on ITO/PEN substrate.

*Electrical characterizations*: The current density-luminance-voltage (J-L-V) characteristics, EQE, and EL of QLEDs are collected using a computer-controlled Keithley 2400 source meter and a luminance meter (Minolta CS-100A). The EL spectra were recorded using a fiber-optic spectrometer (K-MACSV 2100).

<u>Atomic Force Microscopy</u>: A Bruker Dimension Icon working in peakforce mode is used. MPP-11120-10, n doped Si coated conductive tip ( $0.01 - 0.025 \,\Omega$ cm) is used for c-AFM. The conduct mapping via Peakforce tapping mode.

<u>Scanning electron microscopy</u>: A drop of each ink is drop cast onto a Si/SiO<sub>2</sub> substrate and a 5nm gold coating is sputtered onto the surface of the film to reduce electron build-up. Scanning electron microscopy (SEM) images are acquired of the ZnO film using a Magellan 400L SEM operating in secondary electron detection mode using an immersion lens and through-lens-detector (TLD).

<u>Hole-only device fabrication</u>: The hole-only device is fabricated on bare ITO coated glass. The conductivity of the anode is around ~20  $\Omega$ /sq. The PEDOT: PSS (AI 4083) is spin-coated on the ITO substrate, after 60s O<sub>2</sub> plasma treatment, used as a hole injection layer (HIL). The PEDOT:PSS coated ITO substrate is baked at 150 °C for 30 min in air. After then, the PVK:TFB in chlorobenzene is spin-coated at 2000 rpm for 30 s, followed by baking at 150 °C for 30 min, acting as a hole transport layer (HTL). The QDs is inkjet-printed and UV exposed for 5 min. Then, MoO<sub>3</sub> (15 nm)/Ag (150 nm) is deposited on the top of the QDs layer as a cathode electrode in a high-vacuum chamber (base pressure of ~  $1.5 \times 10^{-7}$  torr) by using thermal evaporation.

The hole mobility is calculated by space-charge-limited current (SCLC) in the commonly used Mott-Gurney equation [5];  $J = (9\epsilon\mu V^2)/(8d^3)$ 



**Figure S12** EL characteristic of spin coated QLED without PI and with PI in ambient condition. (a) J-V for pristine ink. (b) J-V for QD/PI. (c) Luminance changes after 1000s operation with and without PI for spin-coated film. (d) EQE for pristine and QD/PI. (e) EL spectrum for pristine and QD/PI. (f) Luminance characteristic of printed QLED with pristine ink. (g) Long term operational stability test for inkjet-printed QD/PI. Inset shows 0.99 luminance changed after 4000 s. (h) Long term operational stability test for inkjet-printed QD/PI after 4000 s.



**Figure S13** (a) J-V-L for CdSe/ZnS QLED. (b) EQE verse luminance plot. (c) Transmittance of PEDOT:PSS electrode on PEN substrate. (d) Transmittance and conductivity depending on the coating cycles.



**Figure S14** (a-b) TEM image before (a) and after cross linking reaction (b). (c-d) Intermolecular distance before (c) and after cross linking (d)



**Figure S15** (a) Schematic illustration of c-AFM set up. (b) Height profile of film with and without PI. (c-f) Morphology mapping of film (c, d) with PI and (e, f) without PI.



Figure S16 (a-b) Current distribution (a) without and (b) with PI. (c) I–V profile of thin pristine QD layer.



**Figure S17 Hole only devices** (a) Forward-reverse swing for QDs with and without PI. (b) Forward-reverse-Forward swing for QDs with PI. (c) Forward-reverse-Forward swing for QDs without PI.



Figure S18 Flexible QLED on PEDOT:PSS/PEN.



Figure S19 The SEM image of film (a,b) with PI and (c,d) without PI after 60% tensile strain.

	Material	Luminance (cd/m <sup>2</sup> )	Colour	Substrate	Patterned EL	Bank	ref
1	CdSe@ZnS	3000	Green	ITO/Glass	Х	Х	R6
2	CdZnSe@ZnS	26320	Red	ITO/Glass	Х	Х	R7
3	CdSe@ZnS	> 10000	Red	ITO/Glass	Х	Х	R8
4	PbS@CdS	n/a	NIR	ITO/Glass	0	0	R9
5	CdSe@CdS	12100	Red	ITO/Glass	0	0	R10
6	CdSe@ZnS	12000	Green	ITO/Glass	0	0	R11
7	InP@ZnSeS	3700, 2500, 400	RGB	ITO/Glass, PEDOT:PSS/PEN	0	Х	Ours
	CdSe@ZnS	24000	Red	ITO/Glass,	-	-	
8	InP@ZnSeS (Spin coating)	6000	Green	ITO/Glass	Х	Х	R12

# TABLE S1. Summary of previous studies on inkjet printed QLEDs<sup>[R6-R12]</sup>

### Reference

- [1] P. Levermore, et al., SID Symposium Digest of Technical Papers 47(1) (2016) 484.
- [2] Y. Son, et al., Langmuir 24(6) (2008) 2900.
- [3] D. Soltman, V. Subramanian, Langmuir 24(5) (2008) 2224.
- [4] A.L. Yarin, Annu. Rev. Fluid Mech. 38(1) (2006) 159.
- [5] L. Qian, et al., Nature Photonics (2011) 5 (9), 543
- [6] P. Yang, et al., Adv. Opt. Mater. (2020) 8, 1901429.
- [7] X. Xiong, et al., Org. Electron. (2019) 73, 247.
- [8] L. Xie et al., Small (2019) 15, 1970083.
- [9] G. Azzellino, et al., Adv. Mater. Technol. (2019) 4, 1800727.
- [10] Y.-H. Won, et al., Nature (2019) 575, 634-638.
- [11] C. Jiang, et al., ACS Appl. Mater. Interfaces (2016) 8, 26162.
- [12] D. W. Shin, et al. Adv. Opt. Mater. (2020) 8, 1901362.