Larger area semiconductor detectors based on novel inorganic polycrystalline perovskite materials:

3D printable polymer-perovskite composite radiation detectors

S. Kearney[1], J. Gosh[2], P. Sellin[2], M. Wang[3] and R. Moss[1]

1. University College London, Department of Medical Physics & Biomedical Engineering
2. University of Surrey, Department of Physics
3. University College London, Institute of Materials Discovery

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Background: perovskite detectors

Where are radiation detectors needed? Security Checks, Diagnostic Imaging, Non-Destructive Testing, Nuclear Management etc.

<u>perovskite materials</u> → ABX_3

- High carrier mobility
- Long carrier lifetime
- Low cost materials
- High optical absorption coefficient
- Simple production / processing
- High photoluminescence quantum efficiency

Example perovskites:

- $MAPbI_3$ (hybrid organic-inorganic)
- $FAPbBr_3$ (hybrid organic-inorganic)
- $CsPbBr_3$ (all inorganic)

→ High Z components (stopping power)
Increased stability

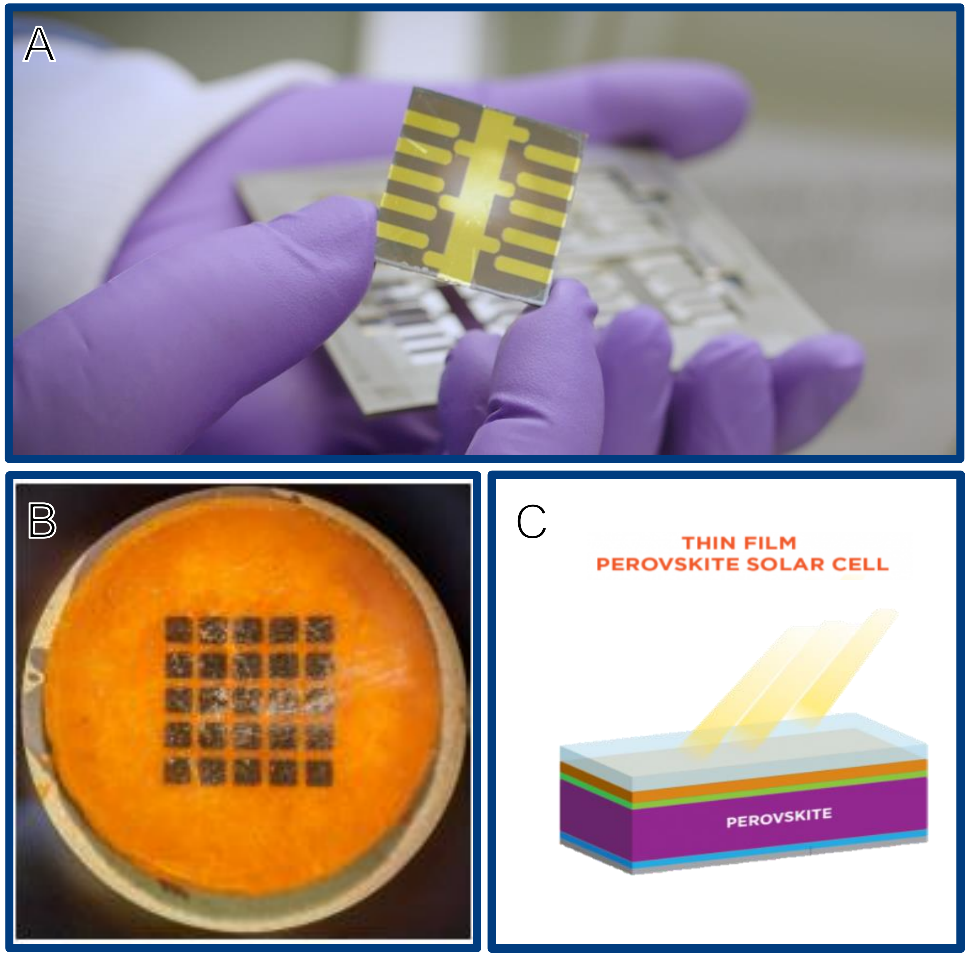


Figure 1: (A) Perovskite thin-film X-ray detector developed at Los Alamos National Laboratory, image taken from physicsworld [1] (B) Image of CsPbBr3 pellet with a 5x5 pixel contact designed by Logan Forth [2] (C) Thin film perovskite solar cell design [3]

[1] Article "Thin-film perovskite detectors could enable extremely low-dose medical imaging" highlight work done by Los Alamos National Laboratory [CITE] https://physicsworld.com/a/thin-film-perovskite-detectors-could-enable-extremely-low-dose-medical-imaging/
[2] Taken from Logan Forths thesis: "An Analysis of the Inorganic Perovskite, CsPbBr3, as an X-ray Detecting Material" [3] Image taken from the U.S. Department of Energy Solar Energy Technologies Office (SETO) webpage "perovskite solar cells" https://www.energy.gov/eere/solar/perovskite-solar-cells

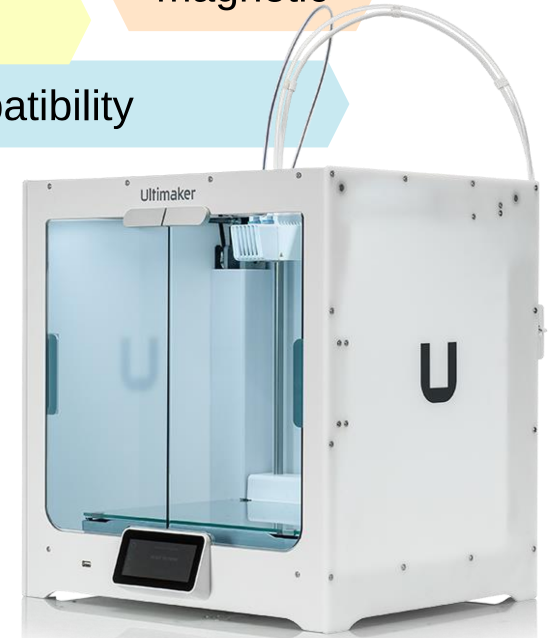
Background: radiation detecting filament

Fused Deposition Modelling (FDM), spools of printing filament are fed into the 3D printer which deposits layers of material by extrusion under controlled temperature and pressure.

Material	T_{melt} (°C)	Properties
PLA	170 – 180	Easy to print, widely available, high strength
ABS	~ 200	Higher temperature resistance, high strength
TPU	~ 225	Flexible
PCL	~ 60	Low printing temperature
Nylon	268	Semi-flexible, high impact resistance

available composite filaments

- electrical conductivity
- metallic finish
- increased strength
- magnetic
- increased flexibility
- biocompatibility



Motivations:

- Custom, complex device designs (e.g. conformal shapes for directional response)
- Availability & lowered costs
- Scalability for large area designs
- Functional 3D printed devices (radiation detection, electrical contacts, signal transmission, housing)

[4] Image taken from https://ultimaker.com/3d-printers

Composite filament: PCL/$CsPbBr_3$

Perovskite material: $CsPbBr_3$

- Forms: single crystal, polycrystalline (powder) or nanocrystal (NC)
- Studies show $CsPbBr_3$ detectors with sensitivities comparable to CdTe detectors [5, 6]

Thermoplastic material: PCL (polycaprolactone)

- Melting temperature / printing temperatures: PLA (210 °C) vs PCL (60 °C)
- Plastic matrix will surround perovskite
- One study produced PCL/$MAPbX_3$ filaments suitable for 3D printing a scintillator detector [7]

Mechanochemical synthesis of $CsPbBr_3$ nanocrystals *(The University of Surrey)*

1. CsBr and $PbBr_2$ are loaded with zirconium oxide balls and milled for 2 h in a planetary ball mill to produce a fine $CsPbBr_3$ powder.
2. Surfactant is added to the milling vial and milled for another 1 h for growth of CsPbBr3 NCs.
3. Finally, the synthesized $CsPbBr_3$ NCs are dispersed in toluene.

[5] Matt, G.J. et al. (2020) "Sensitive Direct Converting X-Ray Detectors Utilizing Crystalline CsPbBr 3 Perovskite Films Fabricated via Scalable Melt Processing". Advanced Materials Interfaces, 7(4), p.1901575. doi:10.1002/admi.201901575.
[6] Di, J., et al. (2021) "Reveal the Humidity Effect on the Phase Pure CsPbBr 3 Single Crystals Formation at Room Temperature and Its Application for Ultrahigh Sensitive X-Ray Detector". Advanced Science, 9(2), p.2103482. doi:10.1002/advs.202103482.
[7] Tang,Y et al.(2022) "In Situ Synthesis of MAPbX3 Perovskite Quantum Dot-Polycaprolactone Composites for Fluorescent 3D Printing Filament." Journal of Alloys and Compounds, vol. 916, 25 Sept. 2022, p. 164961

Sample production

Current test sample fabrication method:

1. PCL pellets will fully dissolved in toluene at room temperature. We dissolve them directly into the $CsPbBr_3$/toluene solution using a magnetic hotplate (~60°C , 300 rpm, 2 hours)

2. $CsPbBr_3$/toluene mixture is sonicated beforehand to prevent colloidal agglomeration.

3. Solution is cast into a custom silicone mold for pellets.

4. Molds are covered with film with several small holes, limiting the dry-rate as the toluene is removed from the material overnight.

5. 15mm circles are cut from the sample centre

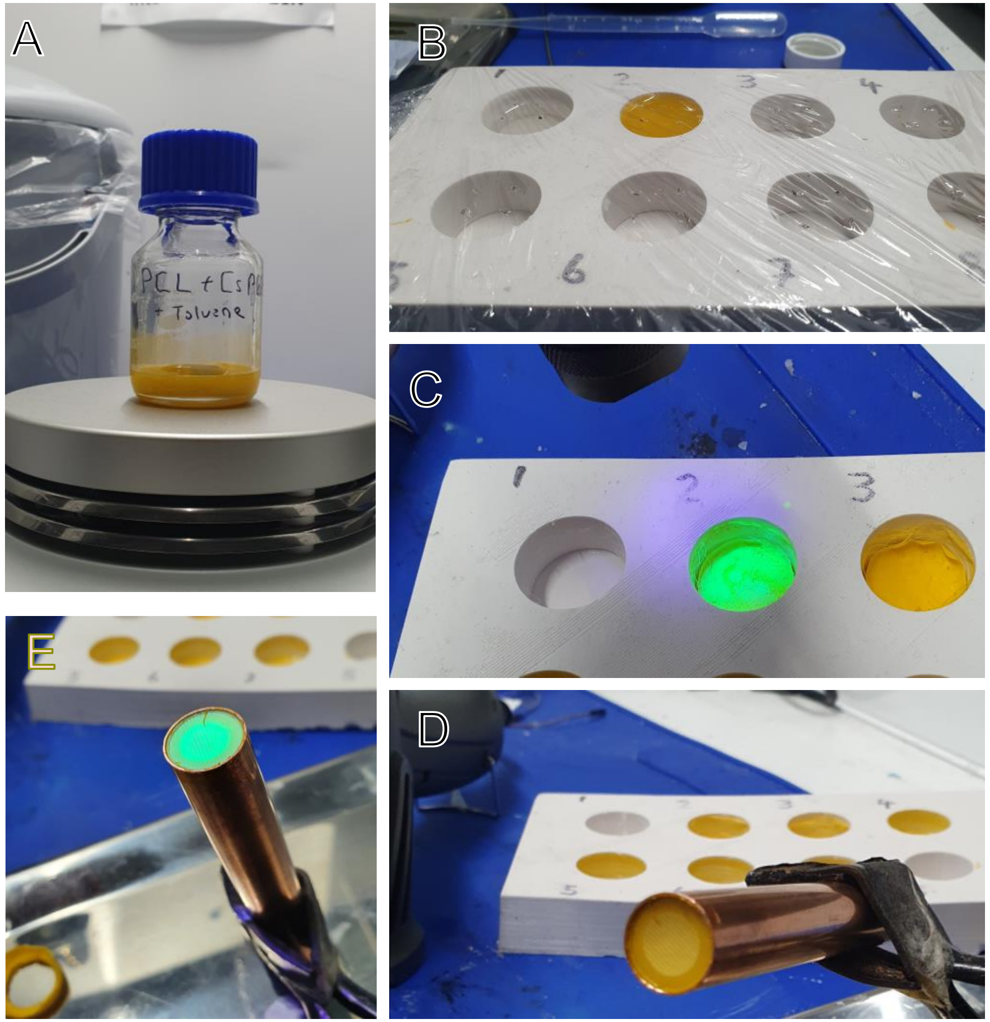
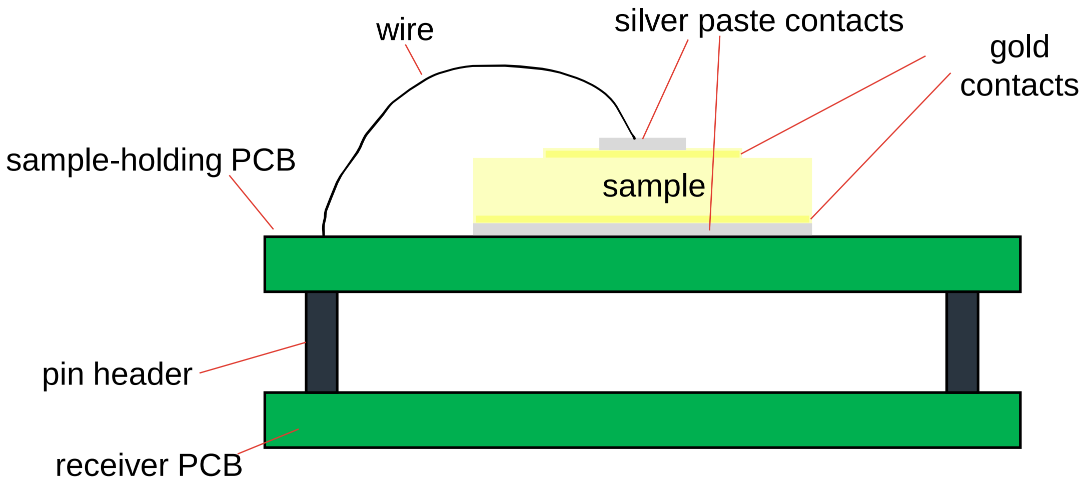


Figure 2: (A) PCL/CsPbBr3/toluene mixture is stirred by magnetic hotplate. (B) PCL/CsPbBr3/toluene solution is cast into silicone mold and covered with film to slow control the solvents drying. (C) A UV light demonstrates the green scintillation the $CsPbBr_3$ material.(D) Further samples are cast. A copper tube has been heated to cut a 15mm circular from the sample centre. (E) UV torch demonstrating scintillation from the circular sample.

Electrical Device Design



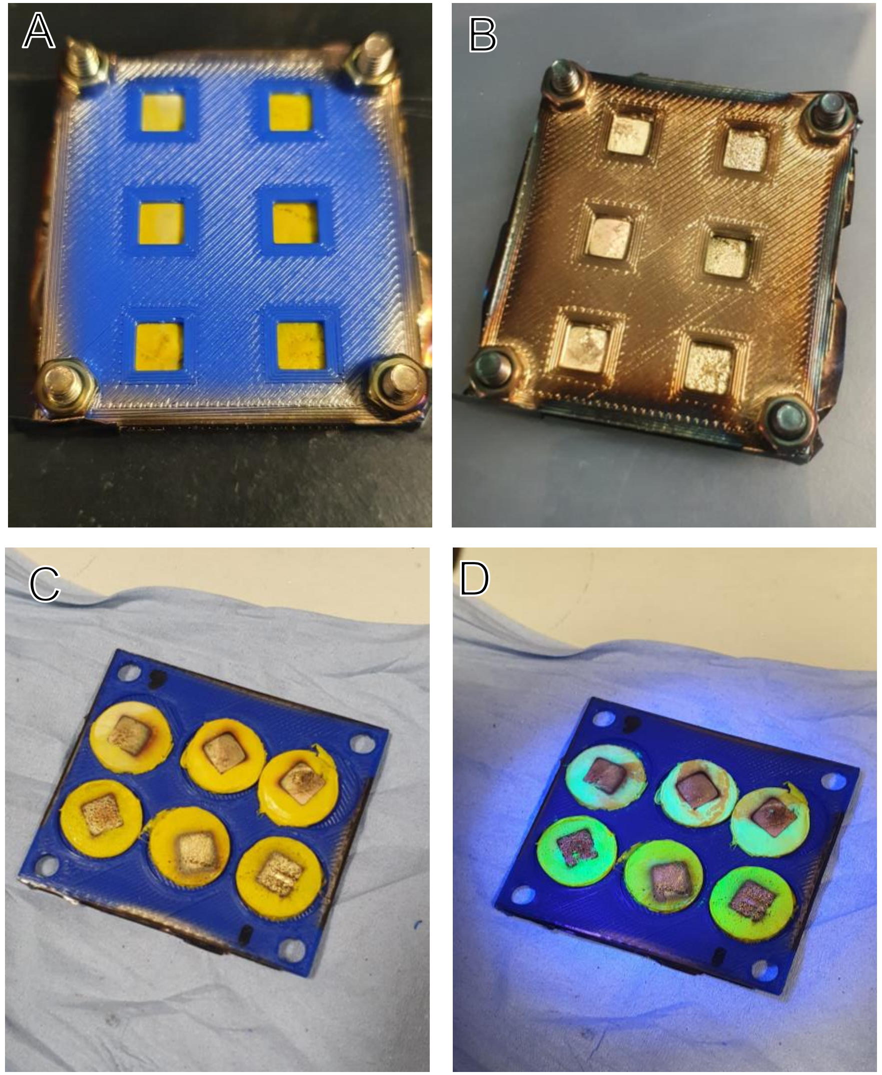


Figure 3: (A) Six samples housed in a 3D printed PLA shadowmask design before the gold contact deposition has been carried out. (B) Six samples following the 100nm gold contacts have been deposited (C) Shadow mask has been opened to reveal the gold contacts. The placement is off for some, while darkening can be seen on all samples (D) UV torch reassures that the perovskite scintillation properties remain.

<u>Device Design:</u>

- PCL/$CsPbBr_3$ samples have 100nm gold contacts deposited via sputtering
- Silver paste is used to mount the samples onto a printed circuit board, and to connect a wire
- This PCB device can now be integrated into our measuring setup (next slide)

X-ray response experimental setup

- Keithley 6487 Picoammeter/ Voltage source
- PCB mounted perovskite device
- R/F shielded enclosure (with lid)
- 15 kΩ short circuit protection resistor

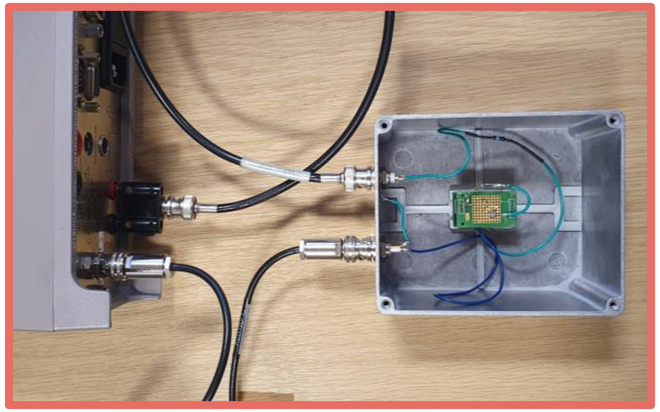


Figure 5: View from above showing the triax and biaxial connections from the Keithley system to the sample enclosure.

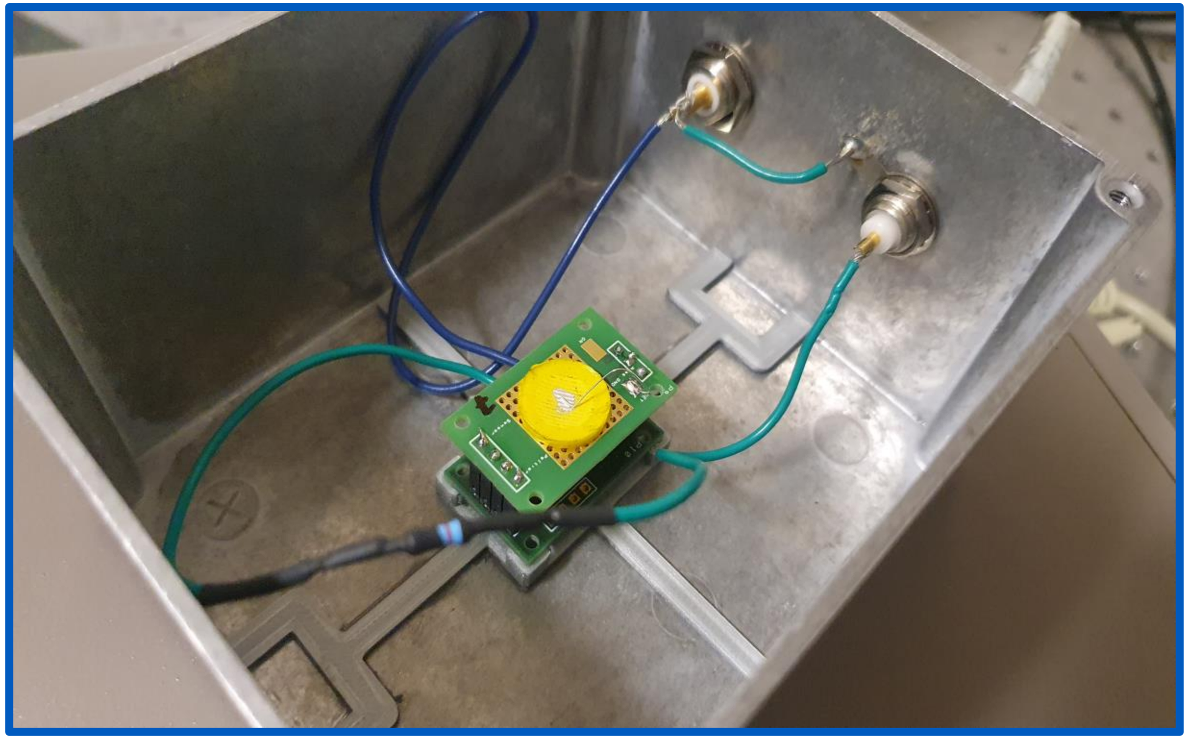


Figure 4: PCL/CsPbBr3 device positioned within the metal enclosure ready for electrical measurements by the Keithley 6487 Picoammeter/Voltage Source

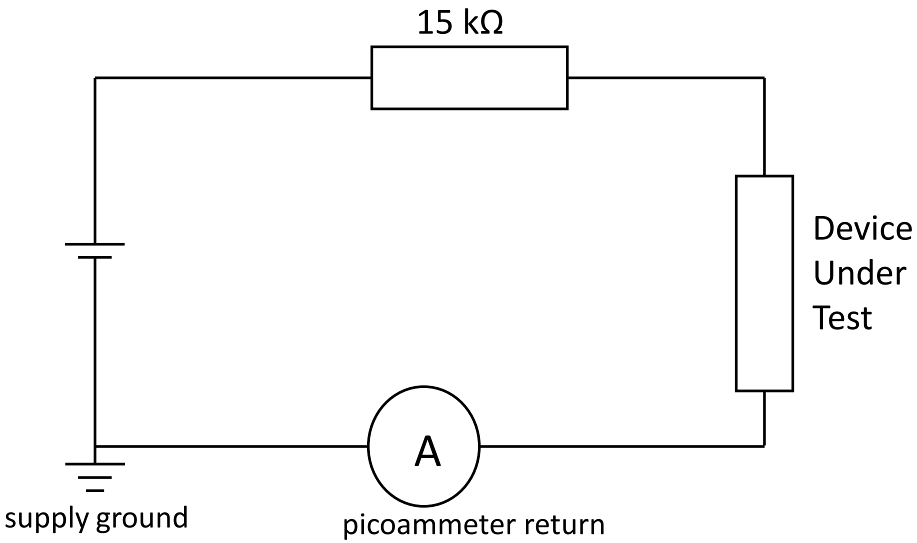


Figure 6: circuit diagram of the picoammter/votlage source, protective resistor and the DUT.

First look at devices

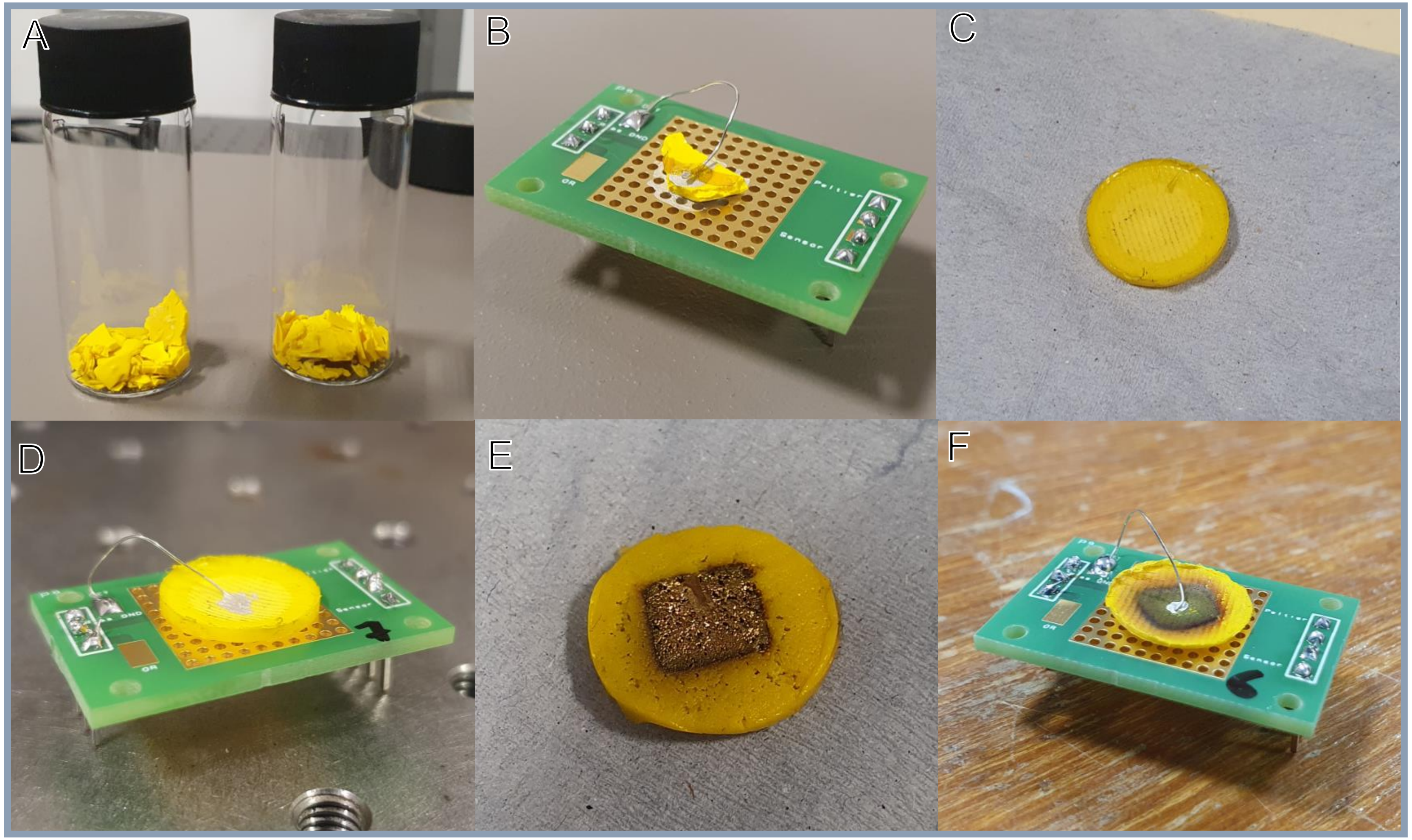


Figure 7: (A) Two vials containing broken fragments of a PLA/$CsPbBr_3$ material made early on (B) The first functioning sample was a PLA/CsPbBr3 fragment mounted on the board using silver paste (C) The PCL/CsPbBr3 sample seen earlier after being cut using the heated copper tube (D) The PCL/CsPbBr3 sample is shown here mounted onto a circuit board, using silver paste without gold contacts (E) Another PCL/CsPbBr3 sample following the gold contact deposition process (F) The same sample has been mounted onto the circuit board, demonstrating the final intended design for photocurrent measurements

Current measurements without X-rays

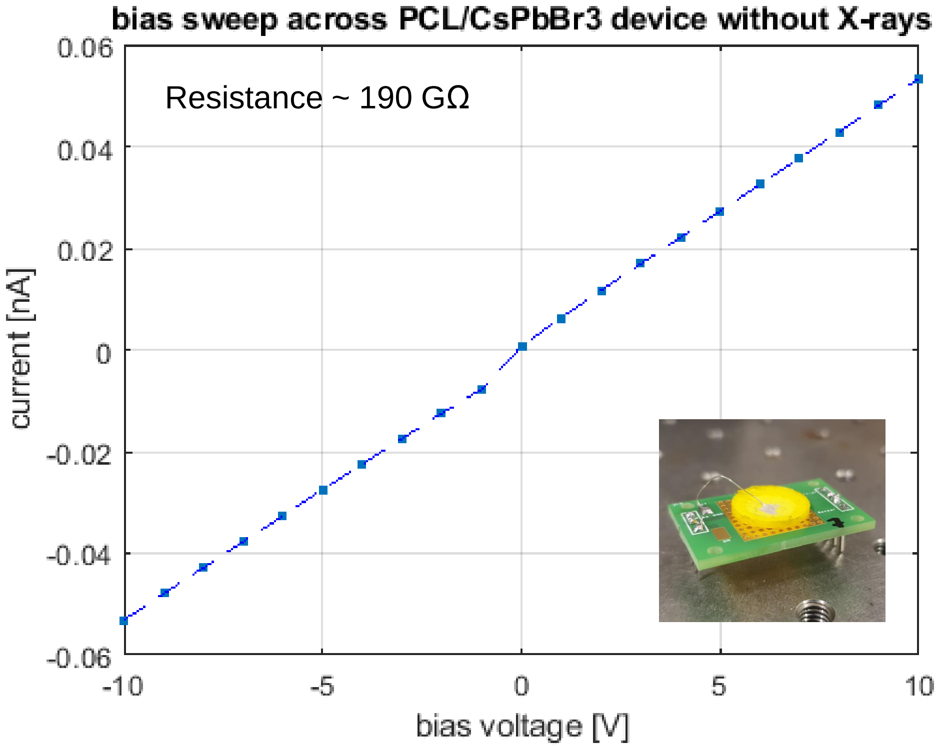


Figure 8: Voltage sweep across the device from -10V to 10V in steps of 1V.

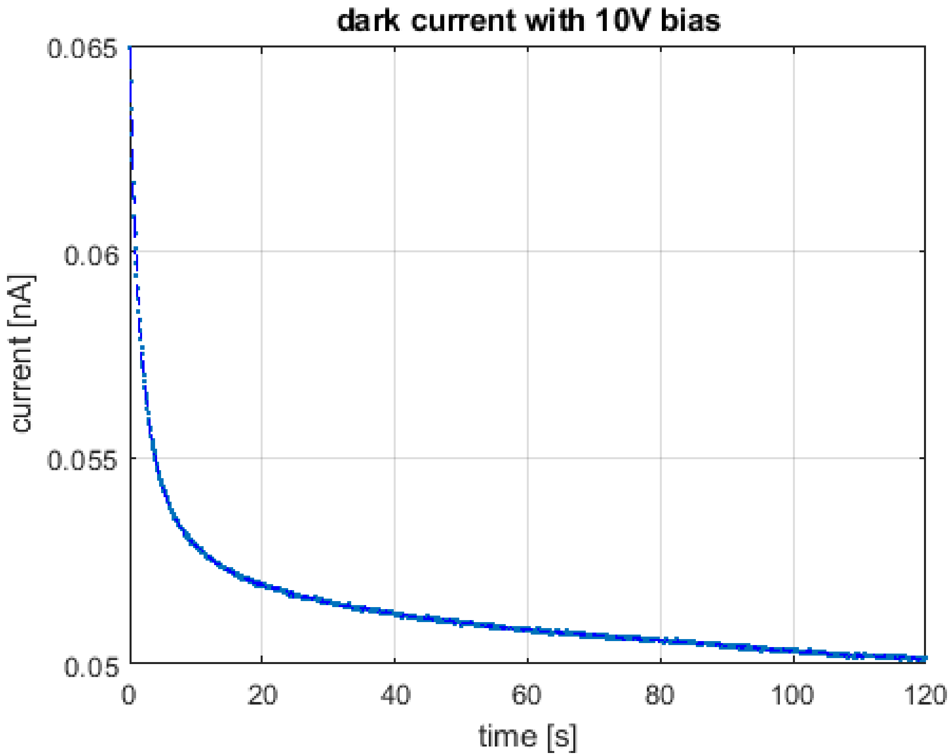


Figure 9: dark current across the device measured over 120 seconds

Device response to X-ray exposure

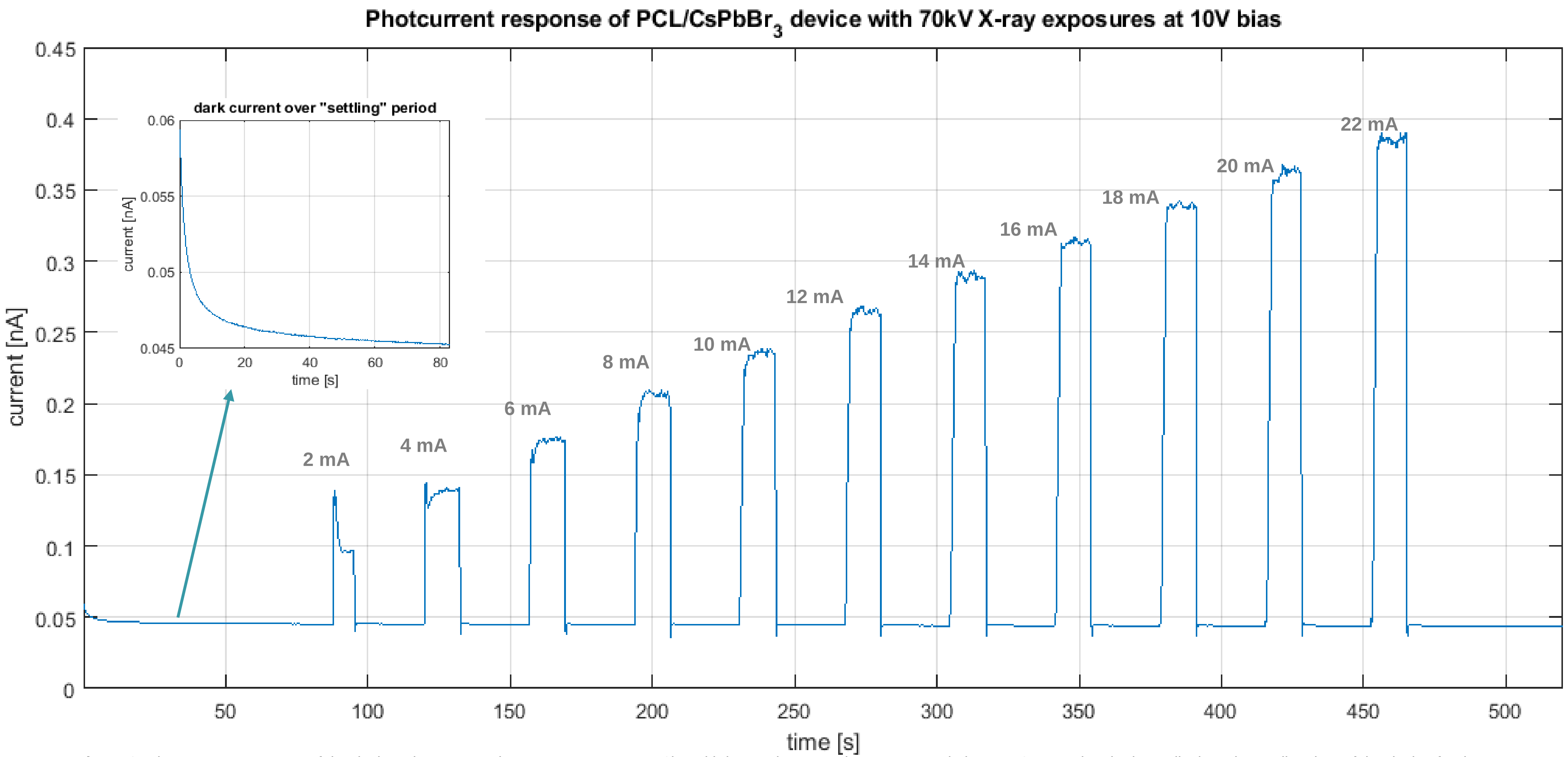


Figure 9: Photocurrent response of the device when exposed to an x-ray source at 70kV with increasing mA values. Measured above 540 seconds. The inset displays the settling time of the device for the first 80 seconds.

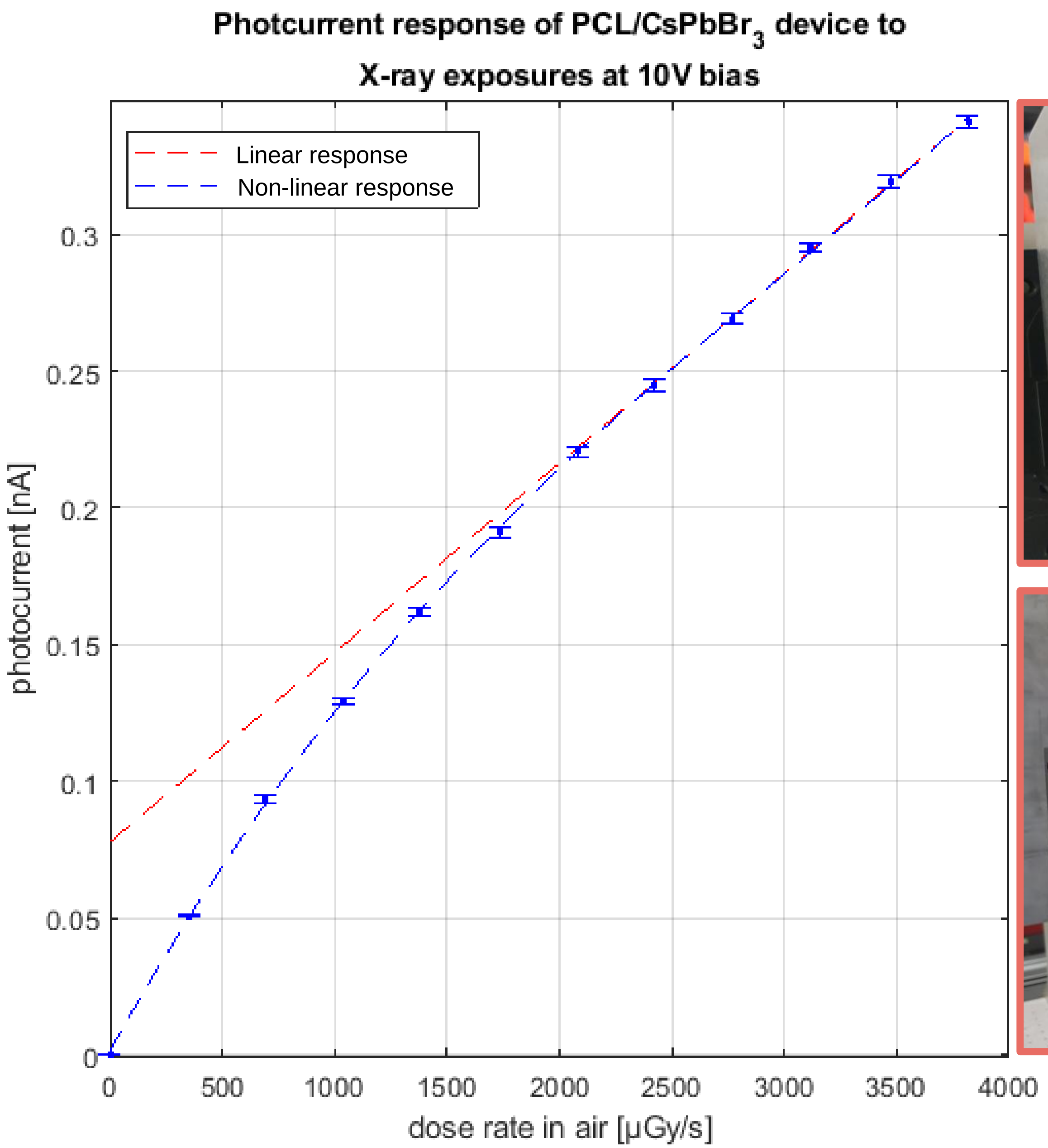


Figure 10: Relationship between the photocurrent response and dose rate in air measured by the Raysafe solo detector.

Relationship between the photocurrent response and the dose rate in air.

Dose rates in air were measured using Raysafe Solo radiation detector.

- Non-linear response at lower dose values
- Linear relationship above ~ 2000 μGy/s

Detector Sensitivity [$\mu C\ mGy^{-1} cm^{-2}$] measurements will be determined by measuring the generated photocurrent for a known area.

Conductivity measurements

<u>**Electrical Percolation Threshold**</u>
The point at which there are sufficient particles to support the electrical networks necessary for conduction.

We can increasing the $CsPbBr_3$ content by controlling the weight %. As perovskite content is increased we expect to move away from electrically insulating behaviour

Initial measurements were inconclusive owing to issues with the gold contact deposition.

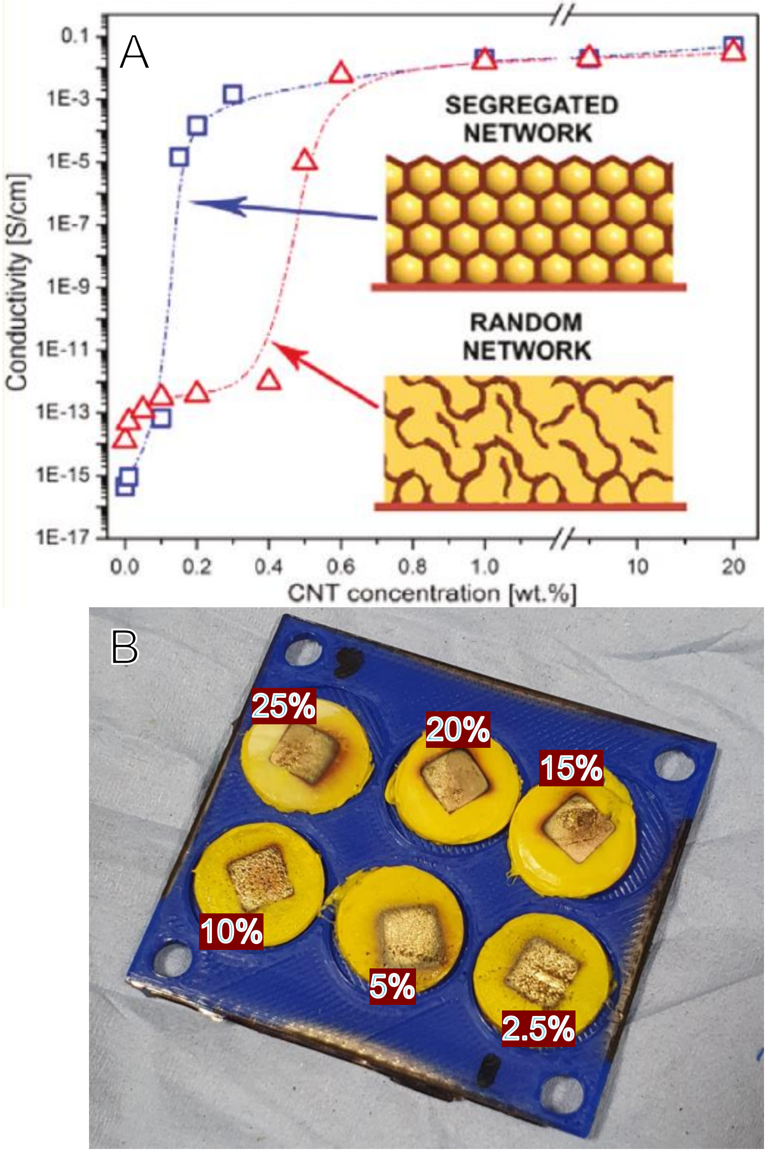
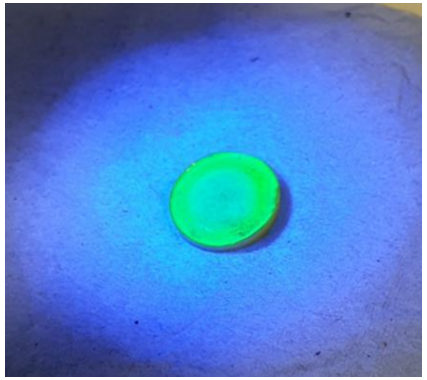


Figure 11: (A) This figure comes from [8], a study into how varying the concentration of carbon nano tubes in a latex matrix will alter the conductivity properties of the material. (A) Six PCL/CsPbBr3 of increasing wt % following gold contact deposition.

[8] I. Jurewicz, et al. "Locking Carbon Nanotubes in Confined Lattice Geometries − a Route to Low Percolation in Conducting Composites." The Journal of Physical Chemistry B, vol. 115, no. 20, 24 Mar. 2011, pp. 6395–6400

Future work: what's next?



Sample Preparation techniques:

- Finetune production of high quality PCL/$CsPbBr_3$ samples.

Material analysis

- Compositional analysis (XRF, SEM)
- Thermal and mechanical resistance
- Radiation Damage

Detector characterisation

- Sensitivity measurements
- Percolation Threshold (conductivity)
- Photoluminescence spectroscopy *(University of Surrey)*

Thank you!

I am happy to answer any questions