Development of flexible radiation detector based of nanomaterials

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Jeong Min Park

Korea Atomic Energy Research Institute

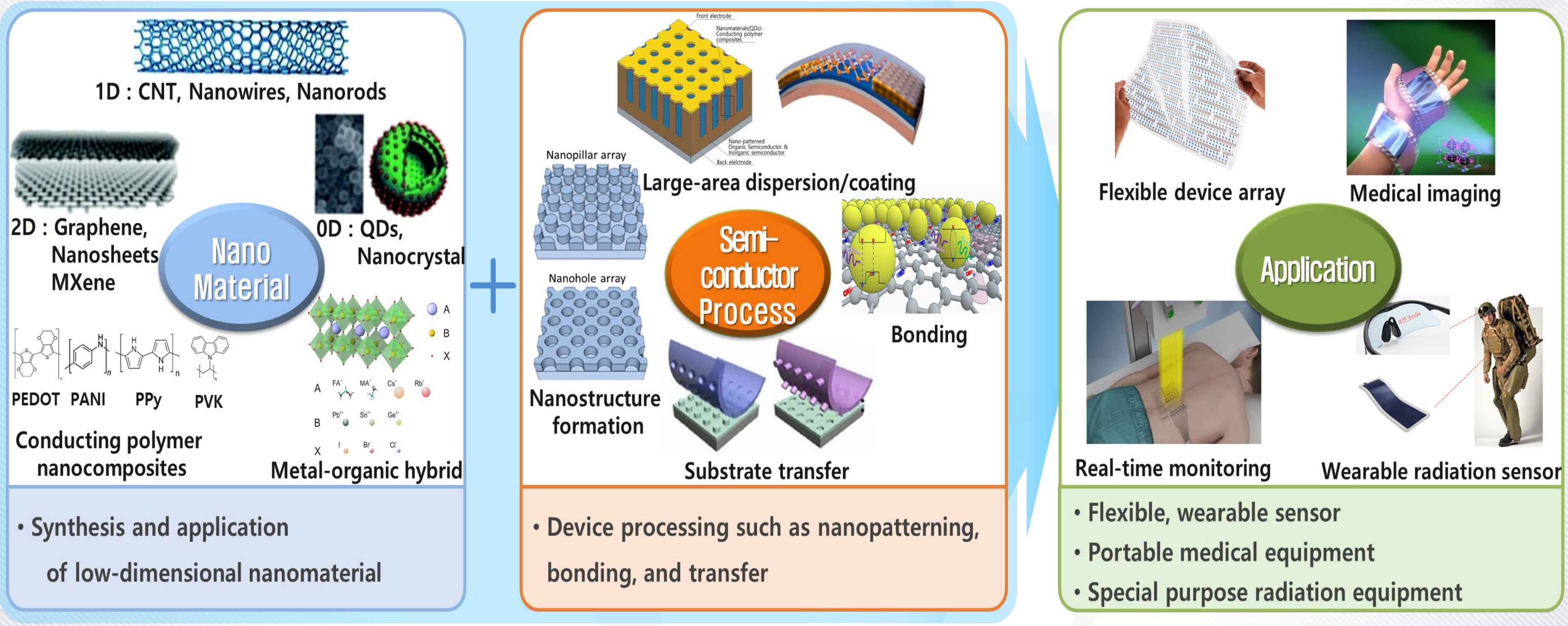
Contents

Development trend of radiation detector

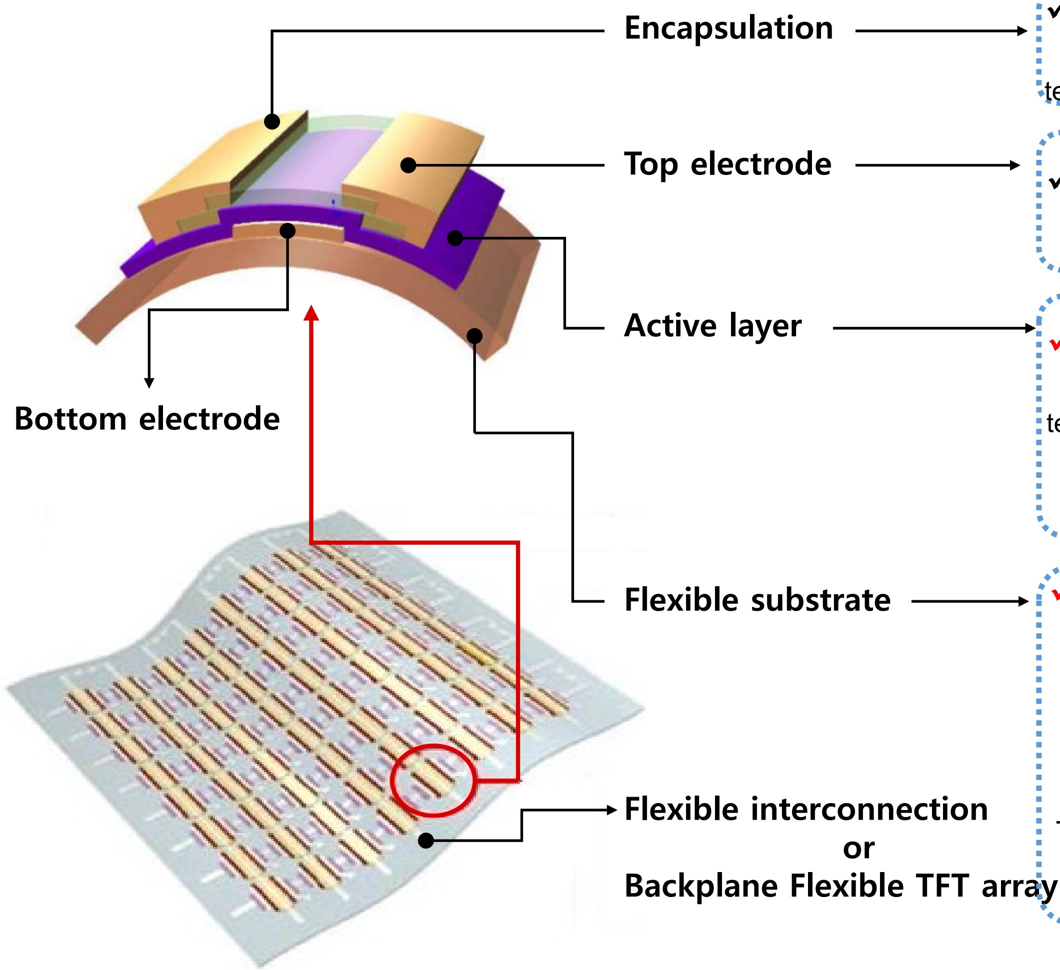
- Advantages of nano-materials based radiation detector
  - Low noise, high sensitivity, miniaturization, low power consumption, large area expansion

Overview

- Goal
  - Develop a high resolution, flexible radiation detector based on nano-materials for medical and environmental applications



» Key element technology



✓ **Encapsulation**

- ALD-based encapsulant layer formation process technology

✓ **Top & bottom electrode**

- Multilayer graphene electrode formation technology

✓ **Active layer**

- Nano-particle synthesis and manufacturing technology
  ($CsPbBr_3$ nanocrystal, PbS QDs)
- Nanomaterial-polymer composite

✓ **Process element technology for device**

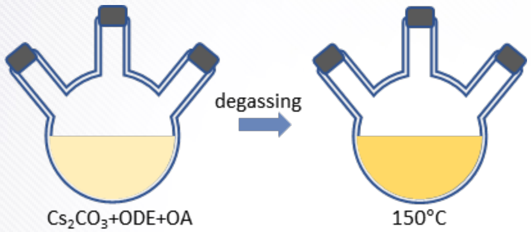
- Graphene transfer technology
- Layer-by-layer nano-material coating technology
- Flexible nanomaterial-polymer composite
- Film processing technology
- Surface modification technology of flexible substrate
- Flexible PCB (F-PCB) device

» Active layers:: $CsPbBr_3$ nanocrystal

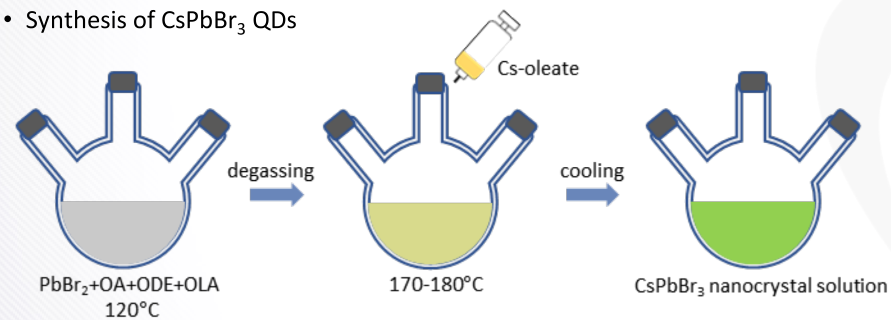
Synthesis of $CsPbBr_3$ nanocrystal for radiation detector

Synthesis and purification (Hot-injection method)

- Preparation of Cs-oleate

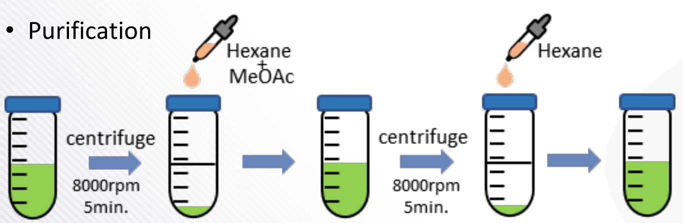


- Synthesis of $CsPbBr_3$ QDs

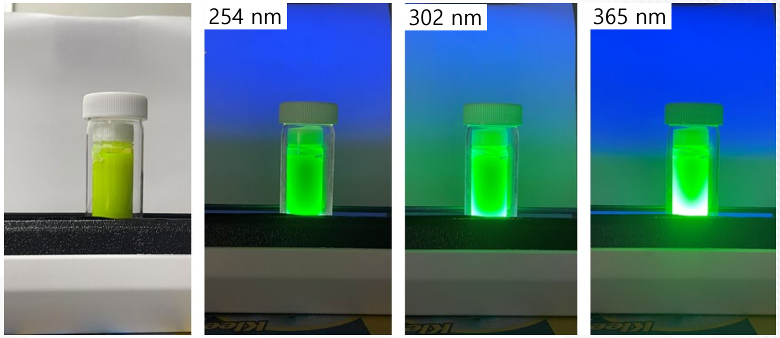


OA : Oleic acid, ODE : 1-Octadecene, OLA : Oleylamine

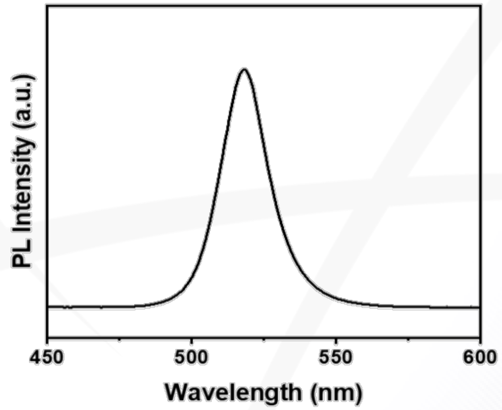
- Purification



Synthesis → Purification → Concentration : 0.5 g/ml $CsPbBr_3$ Nanocrystals



Synthesized $CsPbBr_3$ Nanocrystals



Photoluminescence spectrum

- PL peak position : 518 nm
- FWHM ~ 20 nm

→ Pure green emission

- PLQY ~ 46%

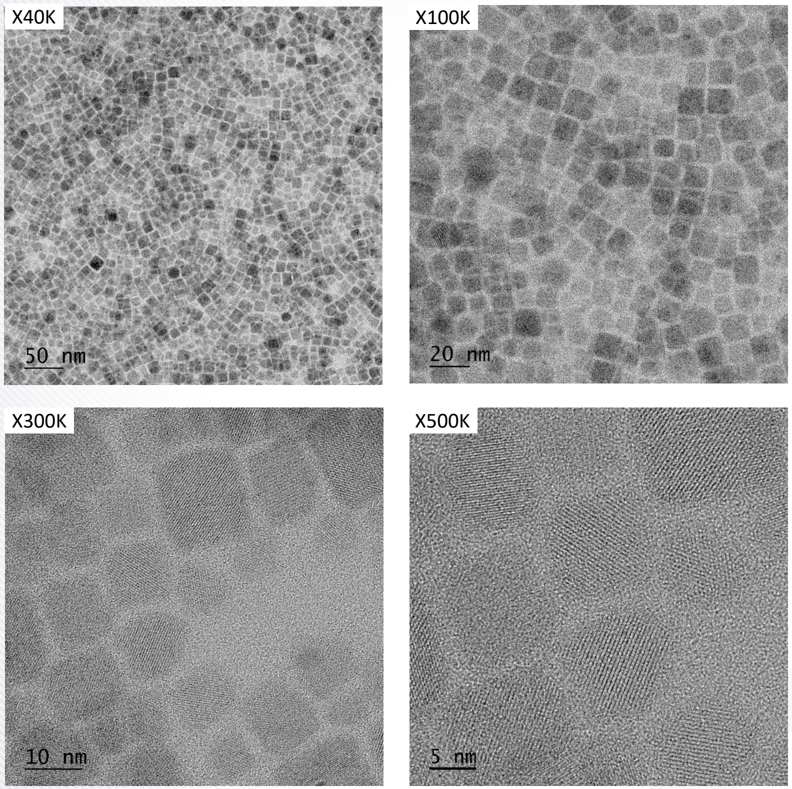
- $CsPbBr_3$ nanocrystals were synthesized using the hot injection method
- The photoluminescence spectrum showed emission peak at 518 nm

» Active layers:: $CsPbBr_3$ nanocrystal

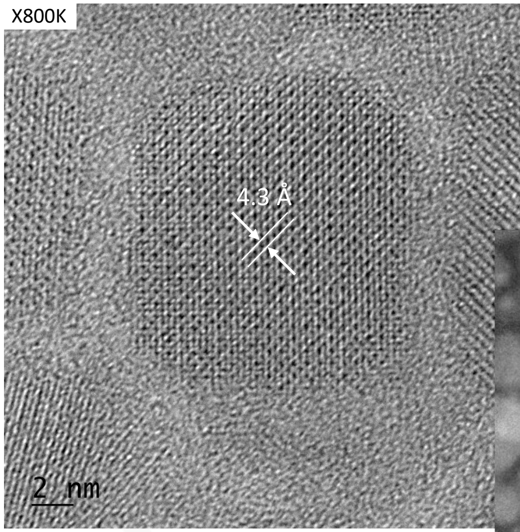
Synthesis of $CsPbBr_3$ nanocrystal for radiation detector

TEM/EDS analysis

*TEM: Transmission Electron Microscopy
EDS: Energy-Dispersive X-ray Spectroscopy

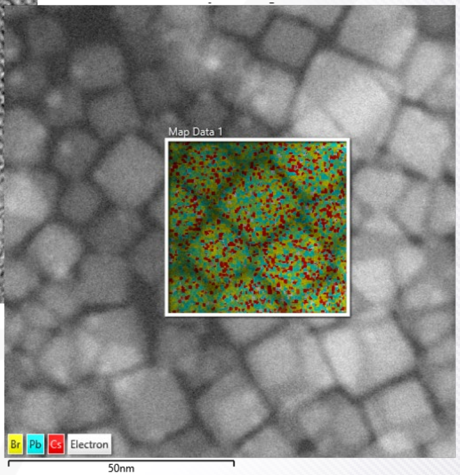


$CsPbBr_3$ nanocrystal size: 9 ~ 17 nm



- Crystal structure : cubic phase
- high crystalline quality
- Lattice spacing : 4.3 Å

EDS analysis image



Element	Line Type	k Factor	Wt%	Atomic %
Br	K series	1.342	33.03	52.05
Cs	K series	39.047	21.38	20.26
Pb	L series	1.750	45.58	27.70
Total:			100.00	100.00

- $CsPbBr_3$ nanocrystals were uniformly synthesized with sizes of 9-17 nm and a lattice spacing of 4.3 Å
- EDS analysis confirmed successful synthesis without impurities

한국원자력연구원 KAERI Korea Atomic Energy Research Institute

» Active layers:: $CsPbBr_3$ nanocrystal

Improvement of optical properties

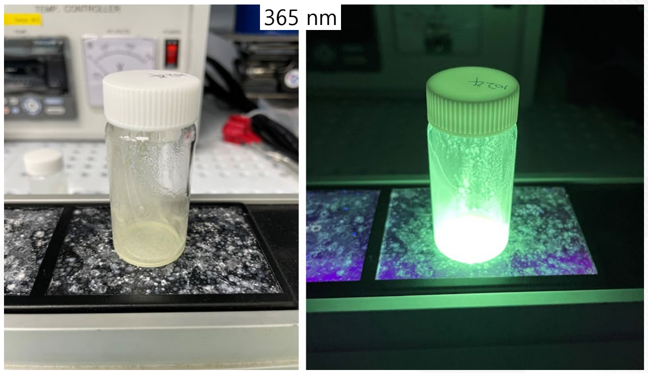
$CsPbBr_3$ nanocrystal powder

① Removal of impurities (Purification/washing)

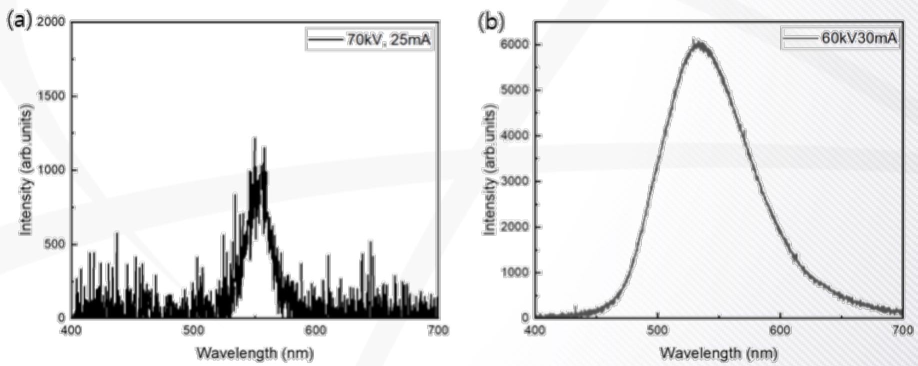
② Powder obtained through vacuum filtration and drying

➡ Obtaining $CsPbBr_3$ nanocrystal powder
: Enhances ease of polymer processing and improves material properties

Improvement of Optical Properties



$CsPbBr_3$ nanocrystal powder under 365 nm excitation



Comparison of $CsPbBr_3$ nanocrystal (a) solution and (b) powder radioluminescence

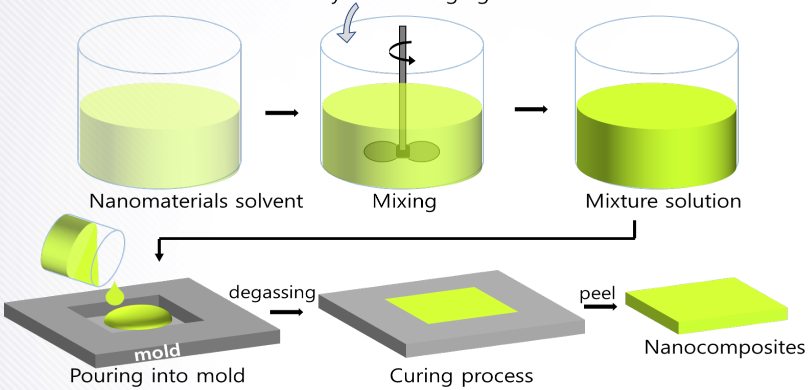
- The synthesized $CsPbBr_3$ was purified and converted into a powder form to facilitate sample preparation
- The $CsPbBr_3$ powder showed ~4.5 times higher radioluminescence intensity than solution

*Polydimethylsiloxane

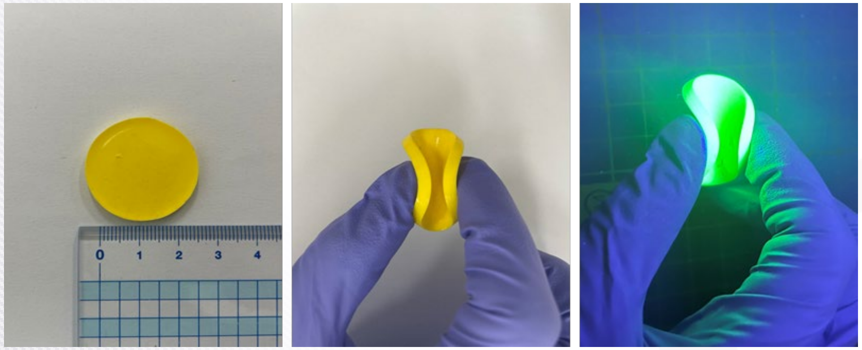
Process element technology for device:: Nanomaterial + PDMS*

Nanomaterial-PDMS polymer composite film fabrication

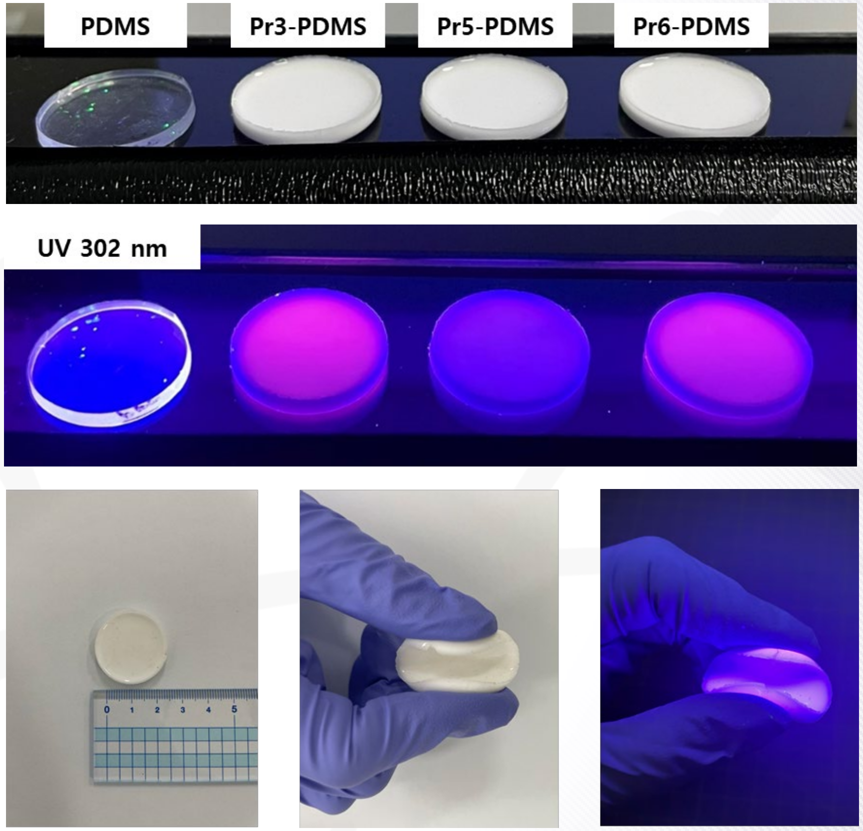
Nanomaterial-PDMS polymer composite film (Molding process)



Process of nanomaterial-polymer composite film



$CsPbBr_3$ nanocrystal-PDMS polymer composite film



Pr doped phosphor-PDMS polymer composite film

- $CsPbBr_3$ nanocrystal/Pr doped phosphor-PDMS polymer composite films were fabricated using PDMS polymer through a molding process
  - Pr3: $LuGd_2Al_5O_{12}$ + Pr_2O_3, Pr5: $Lu_2GdAl_3Ga_2O_{12}$ + Pr_2O_3, Pr6: $Lu_2GdAl_5O_{12}$ + Pr_2O_3

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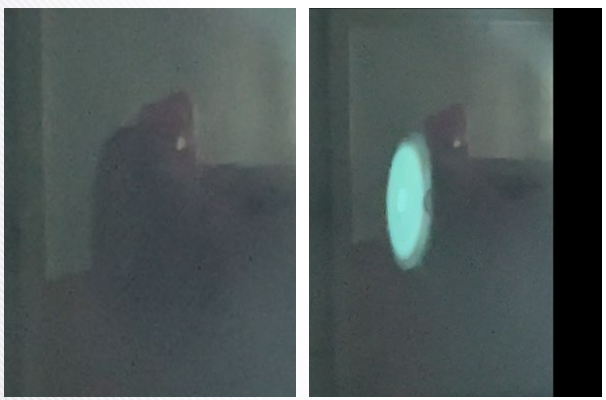
» Process element technology for device:: Nanomaterial + PDMS

Radioluminescence of nanomaterial-PDMS polymer composite films

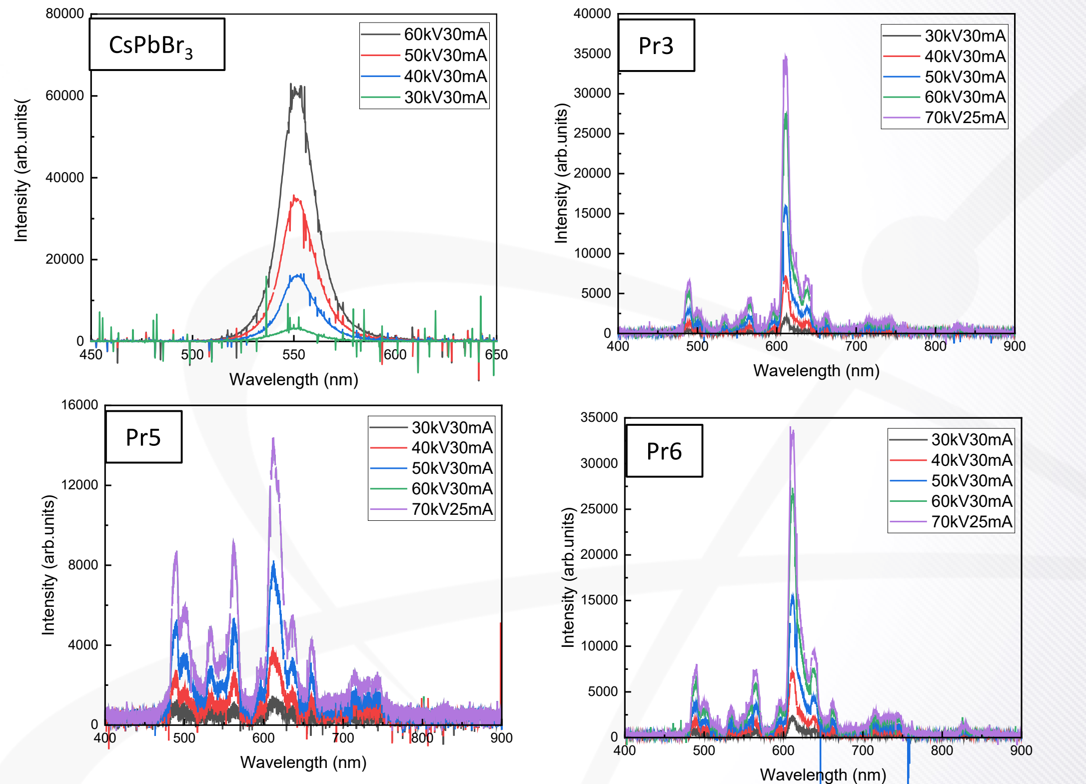
X-ray excited radioluminescence of nanomaterials-PDMS polymer composite films

*Korean Association for Radiation Application

ISO certified X-ray generator (KARA*)



Photograph of luminescence



Luminescence spectra of nanocrystal/Pr doped phosphor-PDMS polymer composite films

- X-ray excited radioluminescence spectra were measured at KARA
  - Voltage: 30-60 kV, Current: 30 mA
- The emission spectra showed similar peaks w/ CsPbBr3 nanocrystal and Pr doped phosphor

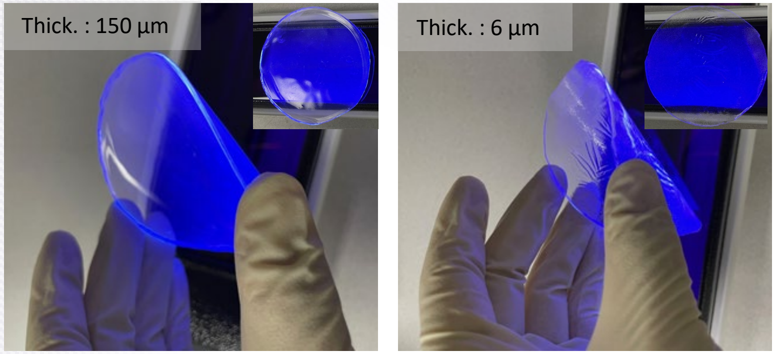
*Polymethyl Methacrylate

Process element technology for device::$CsPbBr_3$-PMMA*

Nanocrystal-PMMA polymer composite film fabrication

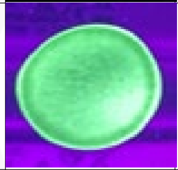
$CsPbBr_3$-PMMA polymer composite film (Molding process)

**relative to the PMMA polymer concentration



4 inch CsPbBr3 nanocrystal-PMMA polymer composite film

Concentration $CsPbBr_3$ nanocrystal-PMMA polymer composite film

	Sample A	Sample B	Sample C	Sample D	Sample E
As					
365 nm UV					
**$CsPbBr_3$ (wt%)	50	50	50	100	100
PPO (g/mL)	none	0.025	0.025	0.025	none
Thick. (mm)	0.3	0.3	0.1	1.3	1.3

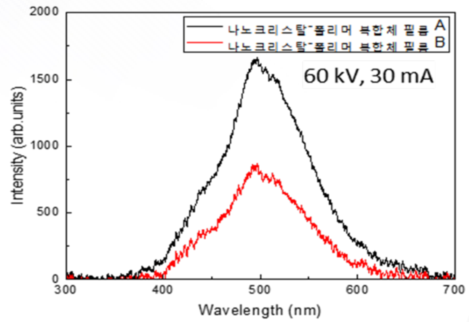
- Fabrication of nanocrystal-PMMA polymer composite film with varying composition and thickness

- Nanocrystal-polymer composite film was fabricated using PMMA polymer through a molding process
- The sample with high $CsPbBr_3$ concentration and no PPO showed the brightest luminescence under 365 nm UV light

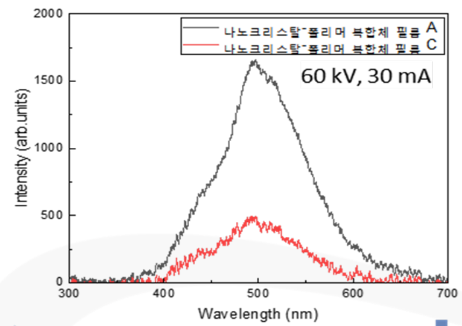
» Process element technology for device::$CsPbBr_3$–PMMA

Radioluminescence of $CsPbBr_3$-PMMA polymer composite films

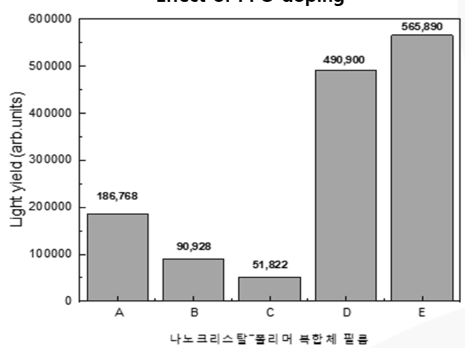
X-ray excited radioluminescence in $CsPbBr_3$-PMMA polymer composite films



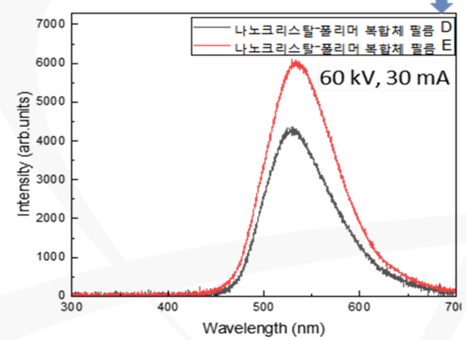
Effect of PPO doping



Effect of film thickness



Comparison of luminescence under different processing conditions



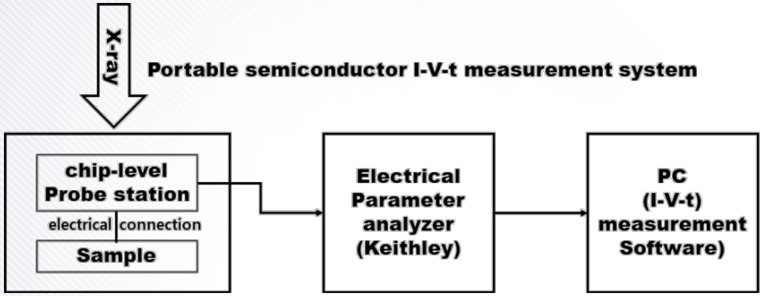
Comparison of luminescence w/ and w/o PPO under optimized film thickness

- To optimize processing conditions, luminescence properties were measured with an X-ray generator @KARA
  - The samples were irradiated with 60 kV, 30 mA X-rays, and luminescence intensity was measured using spectrometer (FLAME-T, Ocean optics)
- The $CsPbBr_3$-PMMA film (Sample E) showed highest luminescence intensity
  - 100 wt% $CsPbBr_3$, No PPO, 1.3 mm thickness

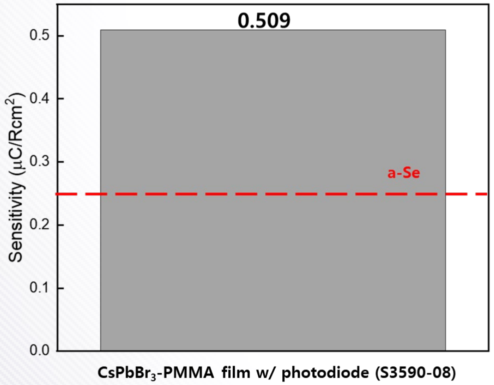
X-ray responsiveness properties::$CsPbBr_3$-PMMA

X-ray responsiveness of $CsPbBr_3$-PMMA composite film coupled photodiode

Sensitivity

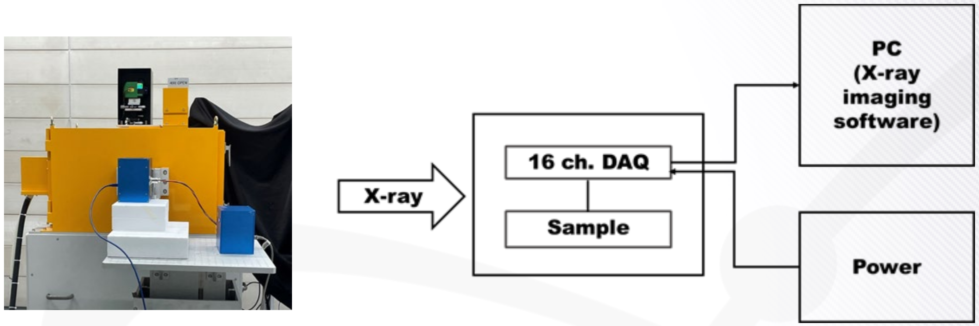


Schematic of sensitivity of measurement system

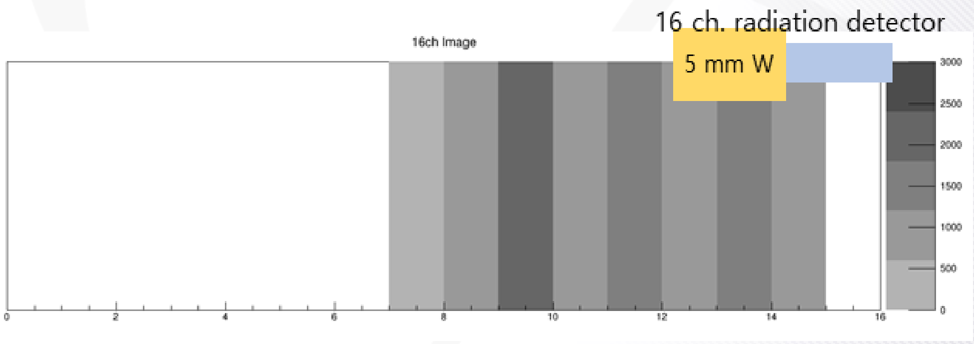


Sensitivity of $CsPbBr_3$-PMMA film (Sample E) coupled photodiode

16 ch. X-ray image



Photograph and schematic of 16 channel X-ray imaging measurement system



16 channel X-ray image of $CsPbBr_3$-PMMA film coupled APD w/ 5 mm W

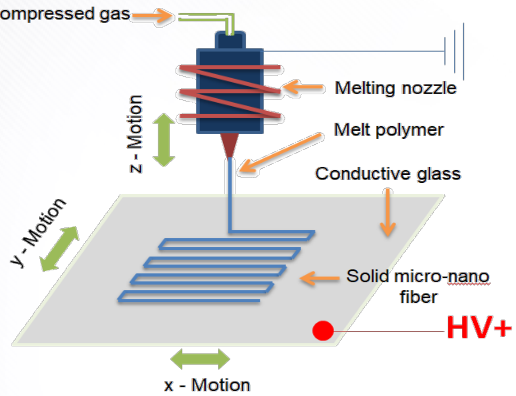
- Sensitivity of the $CsPbBr_3$-PMMA film coupled a PD (SD3590-08, Hamamatsu) was measured under 1.84 R X-rays
  - The charge generated by the PD was measured, and the sensitivity was 0.509 μC/R·cm^2
- 16 ch. X-ray imaging of the $CsPbBr_3$-PMMA film coupled a APD (S15249, Hamamatsu) was measured
  - When half of the detector was blocked w/ 5 mm tungsten and exposed to X-rays, the CsPbBr3-PMMA film coupled APD demonstrated a responsive characteristic to X-rays.

*Polyvinylidene Fluoride

Process element technology for device::$CsPbBr_3$–PVDF*

Nanocrystal-PVDF polymer composite film fabrication

$CsPbBr_3$-PVDF polymer composite film (Electrospinning spray coating method)



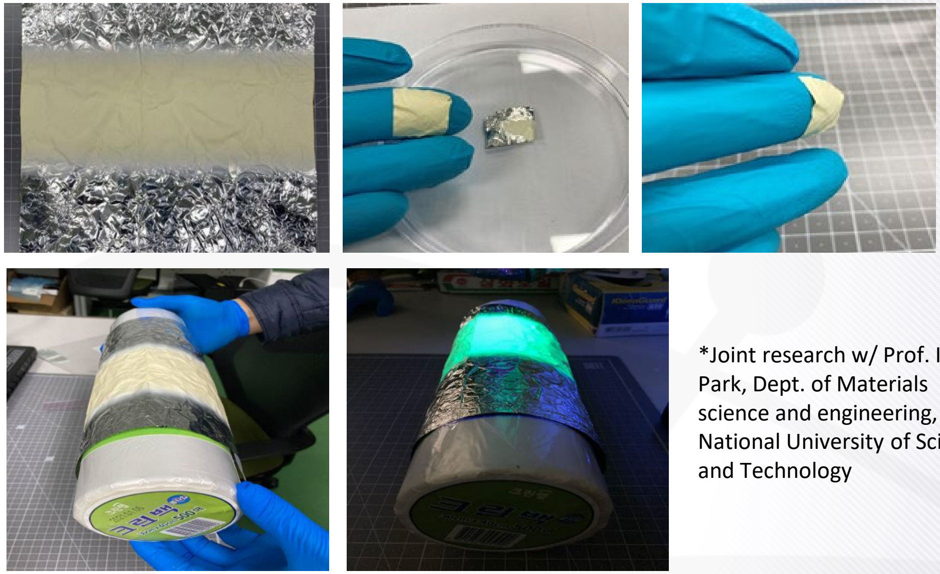
Electrospinning Spray Coating Method

① Mixed w/ $CsPbBr_3$ and PVDF

② Injected at a constant rate using a syringe pump

③ Applied voltage btw nozzle tip and collector plate

→ Mixed polymer solution is electrospun into fibers



*Joint research w/ Prof. Il-Kyu Park, Dept. of Materials science and engineering, Seoul National University of Science and Technology

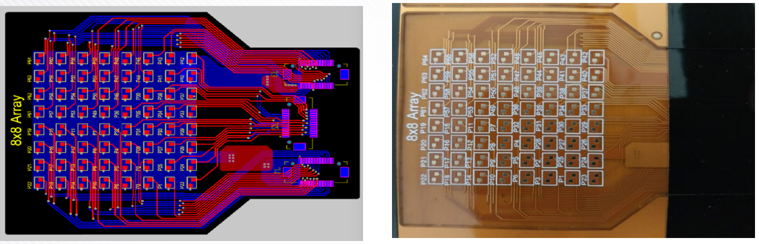
$CsPbBr_3$ nanocrystal-PVDF polymer composite film

- 2.5 wt% CsPbBr3-PVDF nanofiber composite was coated onto a flexible metal foil (25 cm x 25 cm) using electrospinning coating technology
- The film exhibited luminescence under 365 nm UV light
- The electrospinning coating method confirmed the potential of coating substrates of various types, size, and shapes

Process element technology for device::Flexible PCB

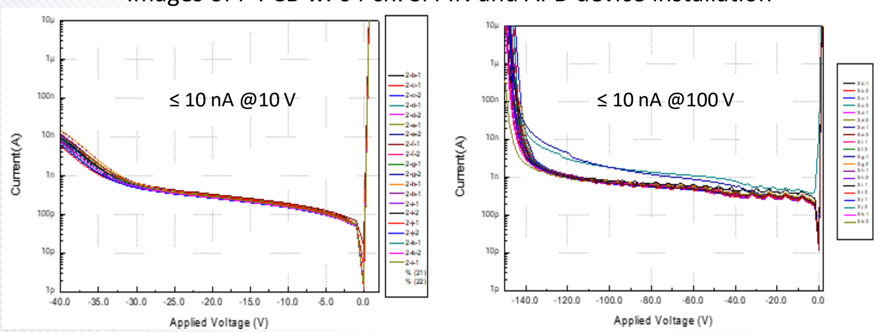
Flexible PCB w/ 64 channel photodetectors

Flexible PCB w/ 64ch. photodetectors



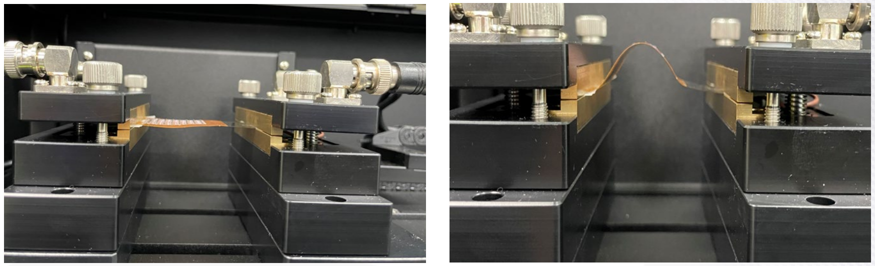
Design and image of F-PCB w/ 64 ch. Si PIN device

Images of F-PCB w. 64 ch. Si PIN and APD device installation

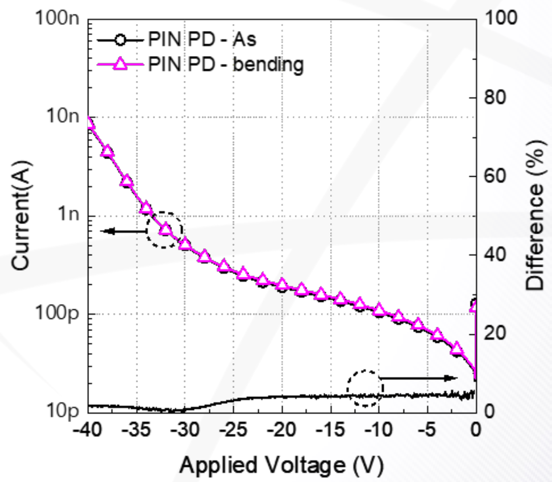


Electrical characteristics of F-PCB w/ Si PIN and APD

Bending properties



Bending test of F-PCB w/ 64 ch. PD (1,000 cycles)



Comparison of electrical properties before/after bending test (1,000 cycles)

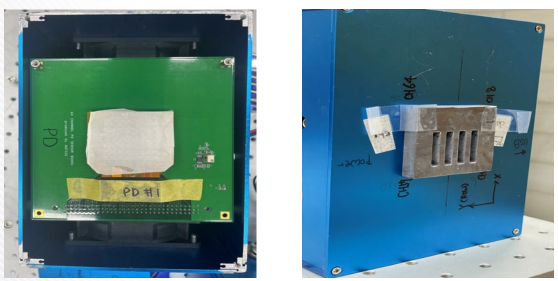
- The F-PCBs w/ 64 ch. Si PIN and APD were developed, respectively
  - Dark current was under 10 nA
- After conducting a bending test w/ 10 mm displacement for 1,000 cycles, the dark current characteristics remained unchanged

X-ray responsiveness properties::$CsPbBr_3$-PVDF w/ F-PCB

$CsPbBr_3$-PVDF polymer composite film coupled F-PCB

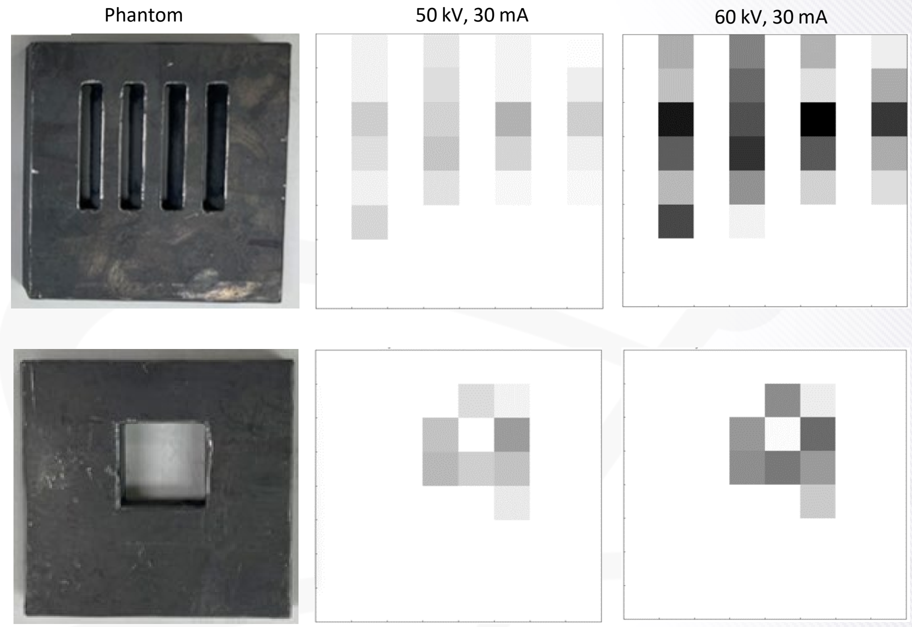
$CsPbBr_3$-PVDF composite film coupled F-PCB

Images of CsPbBr3-PVDF film coupled F-PCB (Si PIN)



Images of CsPbBr3-PVDF film coupled F-PCB w/ DAQ system

64 ch. X-ray image



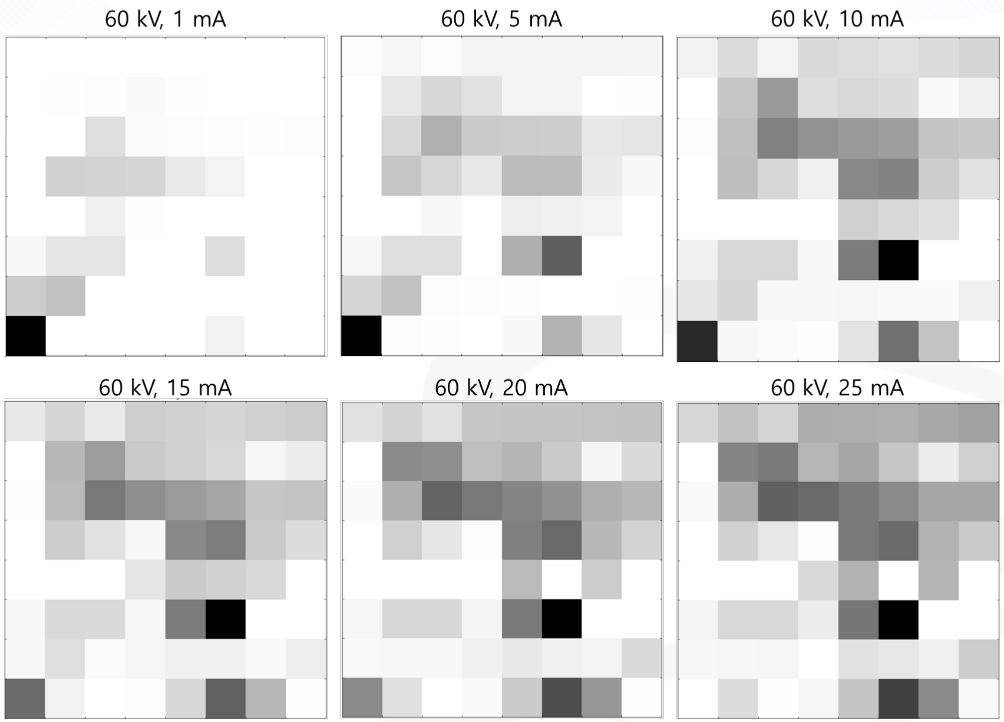
64 channel X-ray images of CsPbBr3-PVDF film coupled F-PCB (Si PIN)

- 50 wt% CsPbBr3-PVDF nanofiber composite was applied onto a F-PCB w/ 64 ch. Si PIN using the electrospinning coating method
- 10 mm thick lead phantom was placed in front of the sensor, and images were obtained under 30 mA, 50 kV/60 kV X-rays

X-ray responsiveness properties::$CsPbBr_3$-PVDF w/ F-PCB

$CsPbBr_3$-PVDF polymer composite film coupled F-PCB

Detection limit



X-ray responsivity of $CsPbBr_3$-PVDF film coupled 64 ch. F-PCB (Si PIN)

- To determine the detection limit, the X-ray voltage was fixed at 60 kV, and the current was adjusted from 1 mA to 25 mA
- X-ray dose on the detector was calculated using SpekCalc program. The X-ray dose was changed from 0.53 mGy to 13.46 mGy
- The CsPbBr3-PVDF film coupled 64 ch. F-PCB Si PIN showed possibility to detect X-rays at doses as low as 2. 69 mGy (60 kV, 5 mA)

Conclusion

- Flexible films were fabricated by combining $CsPbBr_3$ nanocrystals w/ various polymers
- The X-ray sensitivity of the $CsPbBr_3$-PMMA composite film, produced via a molding process, was approximately 0.509 μC/R·cm^2
- The $CsPbBr_3$-PVDF composite was coated on a 64 ch. F-PCB (Si PIN) using electrospinning coating method
    - Phantom images were acquired under 30 mA, 60 kV/50 kV X-ray conditions
    - The $CsPbBr_3$-PVDF film coupled 64 ch. F-PCB (Si PIN) was expected to detect X-rays at dose as low as 2.36 mGy (5 mA, 60 kV)
    - The $CsPbBr_3$-PVDF film coupled F-PCB (APD) is anticipated to capture high-quality images even at low X-ray doses

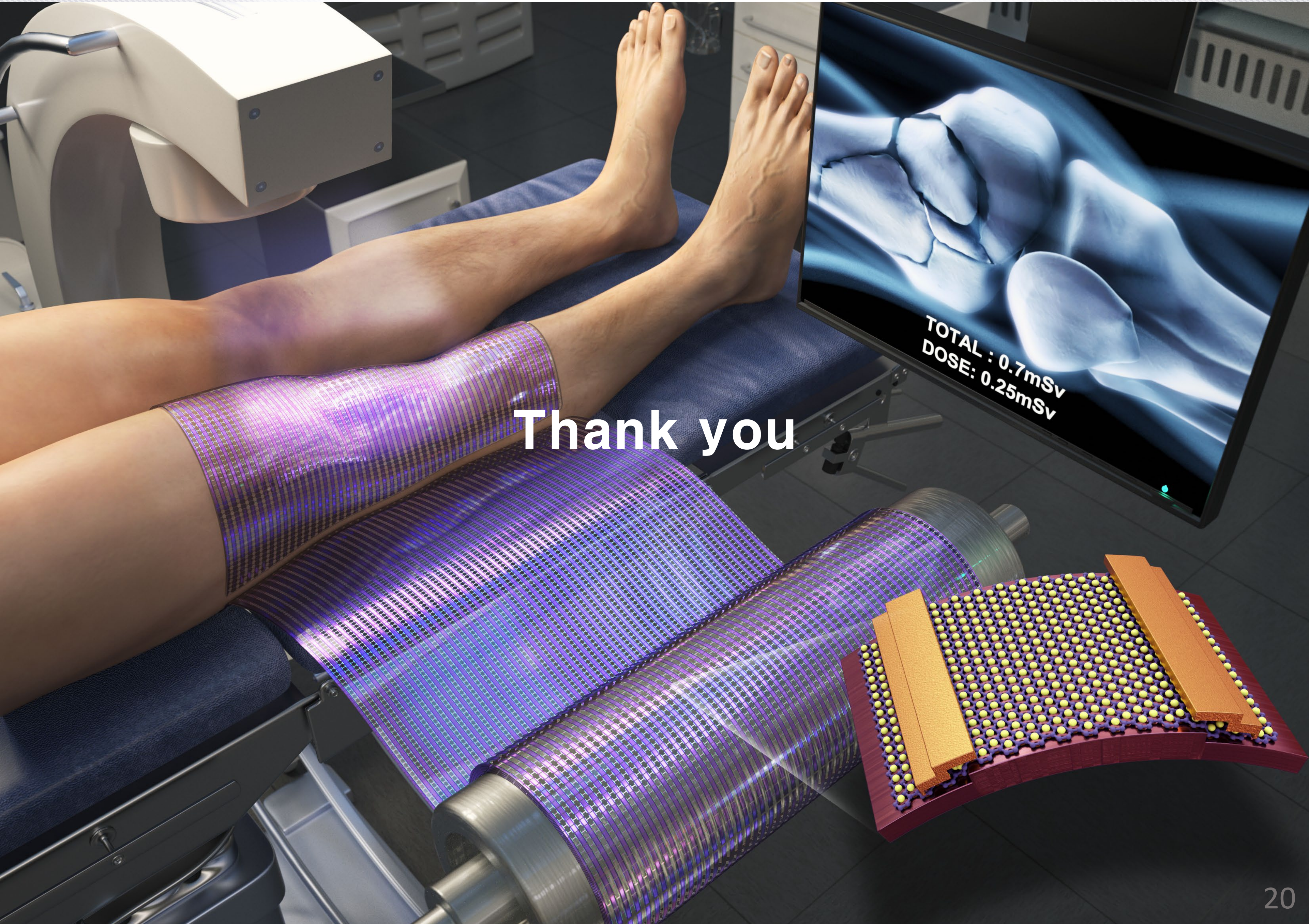
Radiation Equipment Fabrication Center

Photolithography zone
(100 class)

Thermal process, deposition, etching, wet zone
(1,000 class)

Crystal growth and purification room

Characteristics evaluation room


TOTAL : 0.7mSv
DOSE: 0.25mSv
Thank you

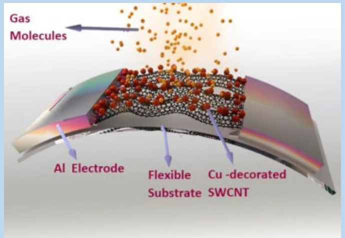
» Trends of research & technology

Flexible Electronics

Display

Flip phone
-SAMSUNG-

Sensor



Gas sensor
-Shiraz university-

Health care

Flexible vital sensor
-IEEE Sensor J.-

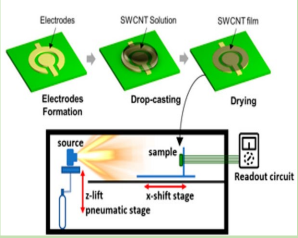
- **Flexible Electronics: Display- Commercialization in progress**
  Optic/Chemical sensor-Early stage research in progress

Nano-material Radiation Sensor

Perovskite scintillator

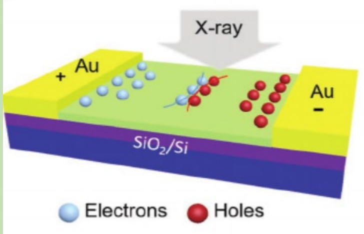
Korea University(2018)

Carbon nanotube



NASA(2019)

Quantum dots



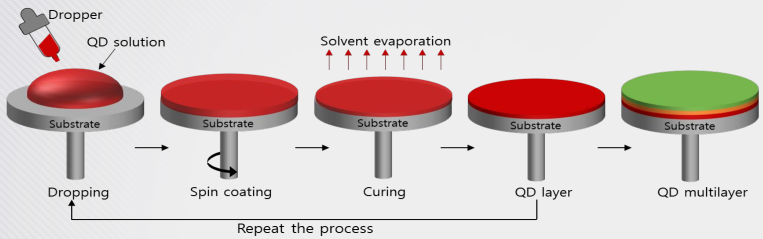
Monash University(2019)

- **Nano-material Radiation Sensor: Direct type-Early stage research in progress**
  Indirect type-Rapid increase in research paper publications

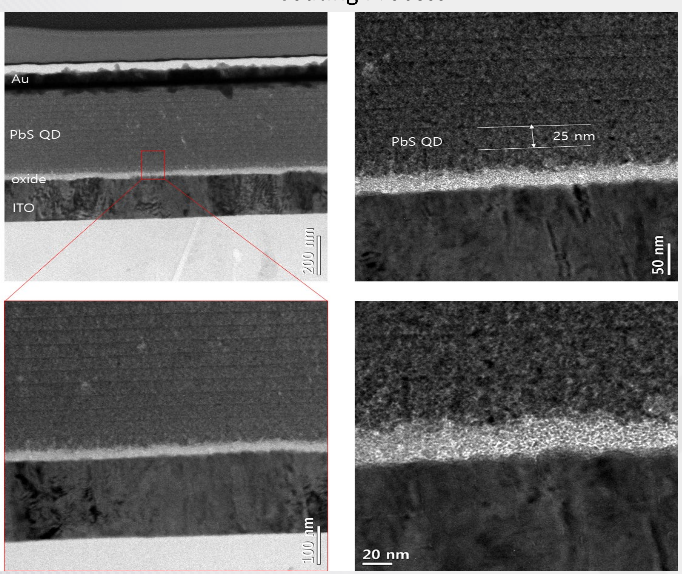
Coating technology

Optimization of nanomaterial coating technology and flexible substrate process conditions

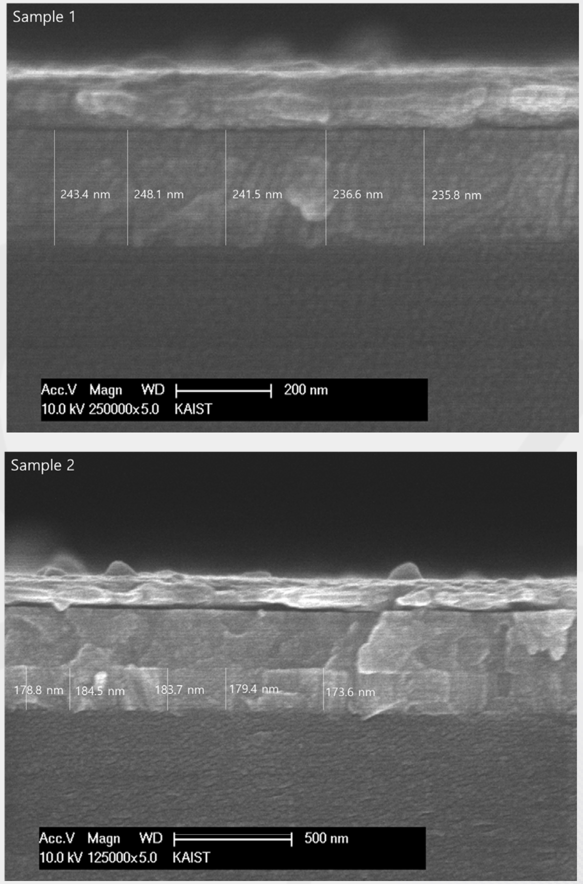
Improvement of LBL (layer-by-layer) Coating Technique



LBL Coating Process



- 13 layers of PbS QD coating (1 layer thickness : ~25 nm)
- Confirmed precise coating conditions for PbS QDs, allowing compatibility with oxide and metal layers for device integration
- Thickness variation within ±5%



- 240 nm target thick.
- Thick. variation
  : average 1.6 %

- 280 nm target thick.
- Thick. Variation
  : average 2.3 %

SEM images of LBL coated multilayer films w/ PbS QDs

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