PHOTONICS RESEARCH GROUP

# Short-Wave Infrared Photodetectors Based on Colloidal Quantum Dots

June 13th 2017

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and Prof. dr. ir. Zeger Hens

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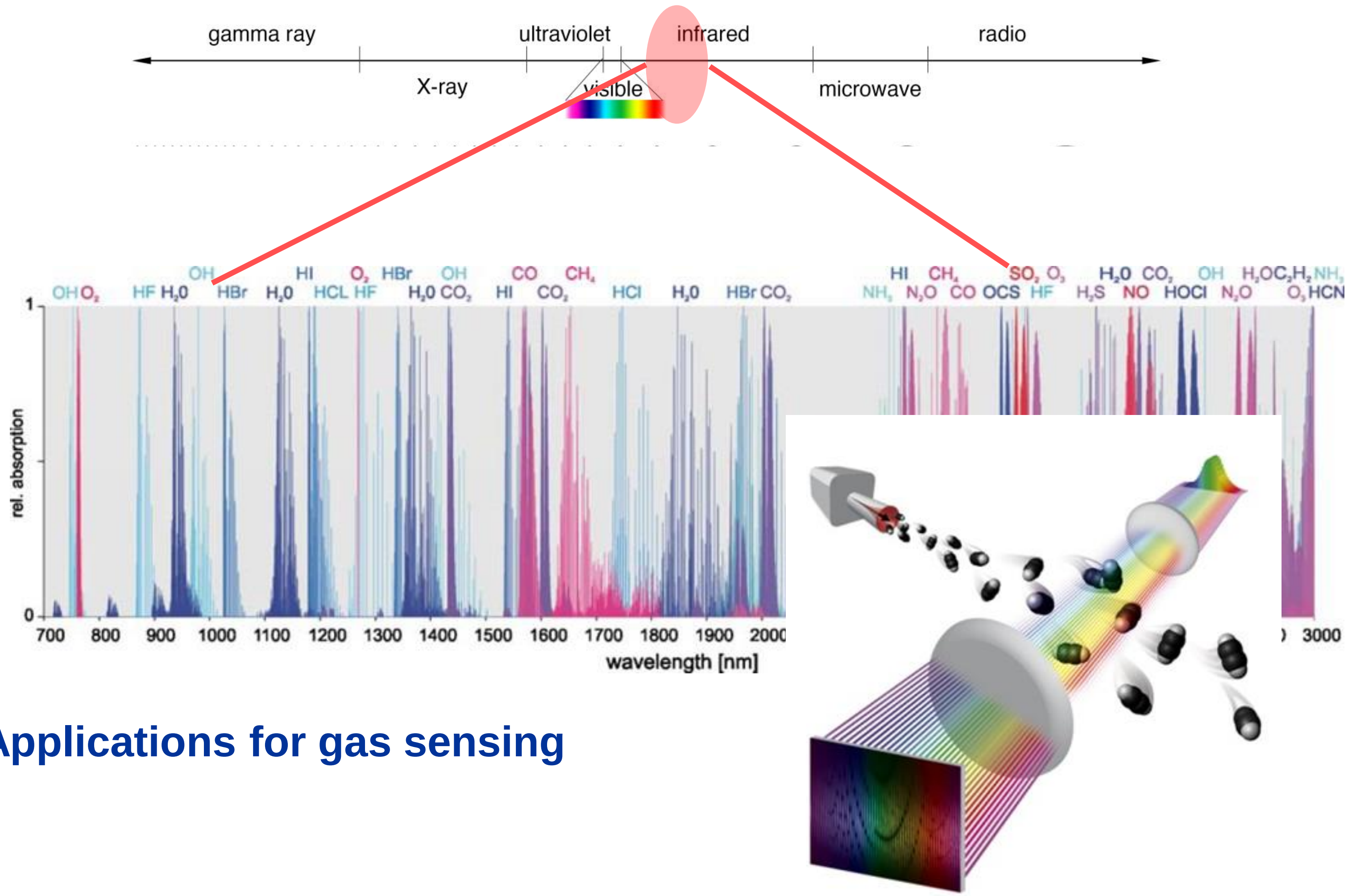
# Why Short-wave infrared detectors based on QDs?

## Short wave infrared: 1-2.5 µm wavelength range

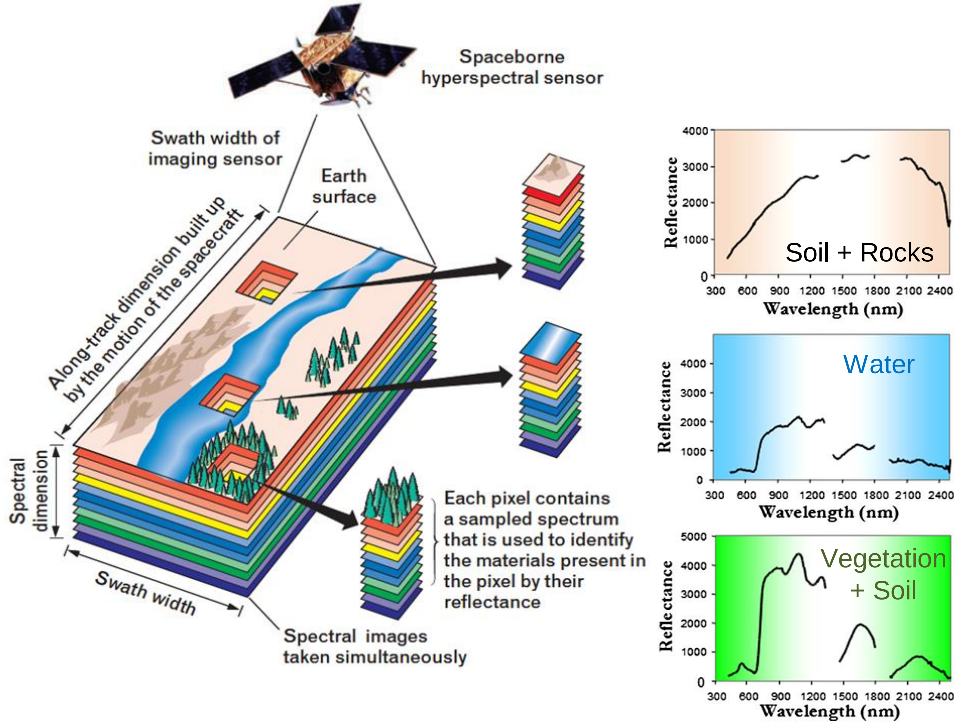



## Applications for gas sensing

# Why Short-wave infrared detectors based on QDs?

**More Applications:**

- Enhanced vision (night vision, through fog)
- Hyperspectral imaging


# WHY SHORT-WAVE INFRARED DETECTORS BASED ON QDS?

**Current technology:**

III-V semiconductors (extended InGaAs based)

epitaxial growth techniques, processes lower yield compared to silicon technology => cost

cost limits the number of applications where these camera's / detectors can be applied (e.g. smart phone)




=> Novel approach avoiding epitaxial growth of semiconductors, integration on 200mm/300mm silicon wafers

=> Performance of a SWIR III-V camera at the cost of a visible CMOS camera?

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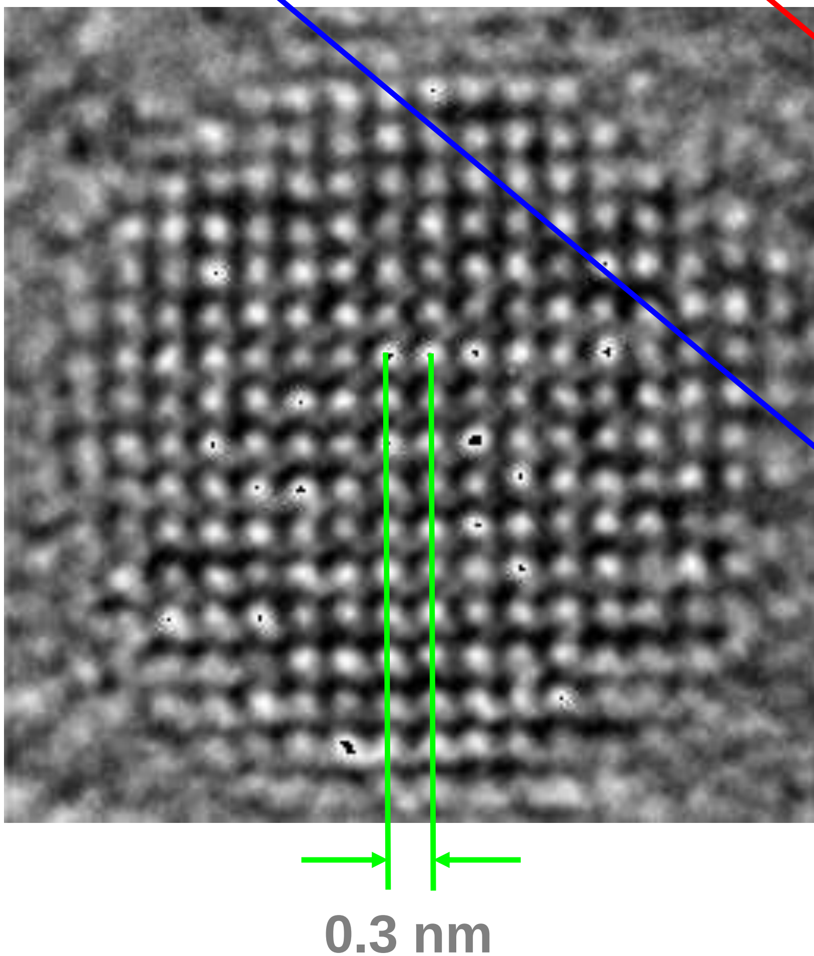
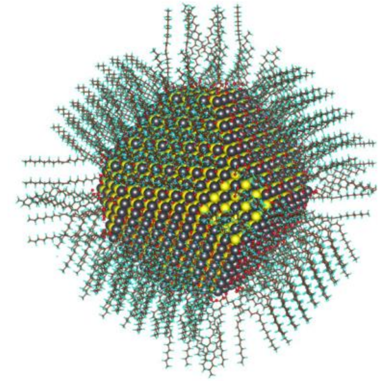
# Colloidal Quantum Dots for SWIR?



**Small box**

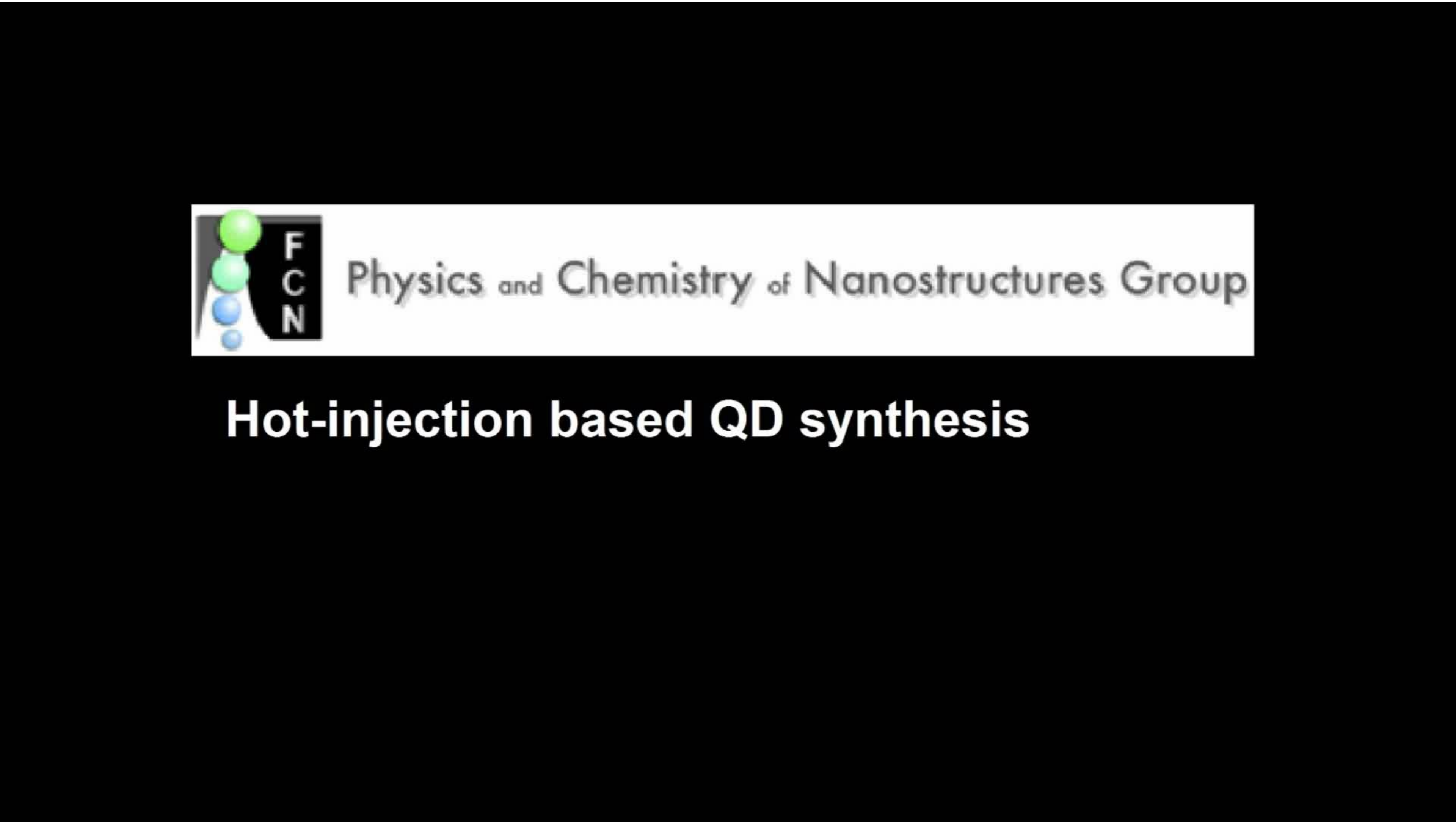
**Confining electrons**

**(In practice a semiconductor nanocrystal)**

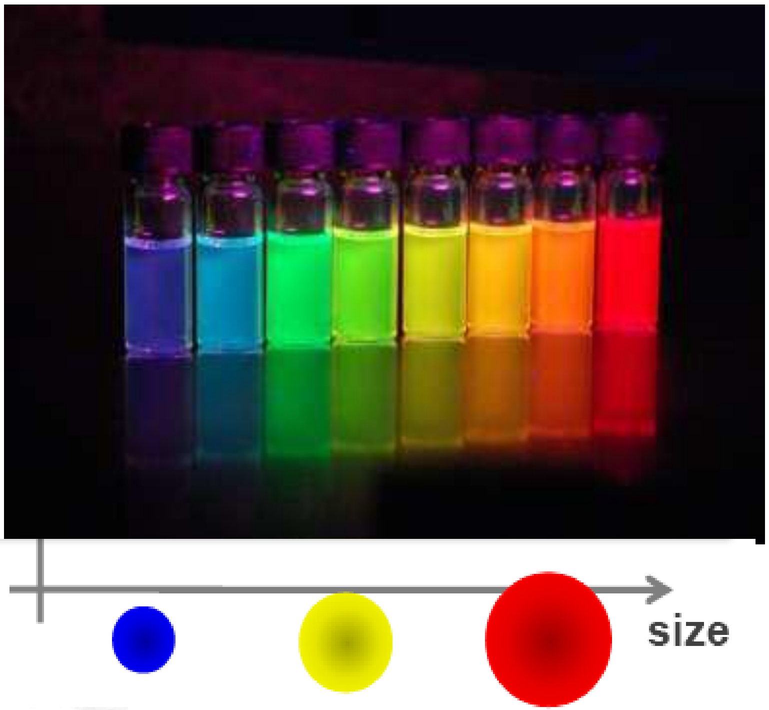
**1-1000 nm sized particle dispersed in a continuous medium**

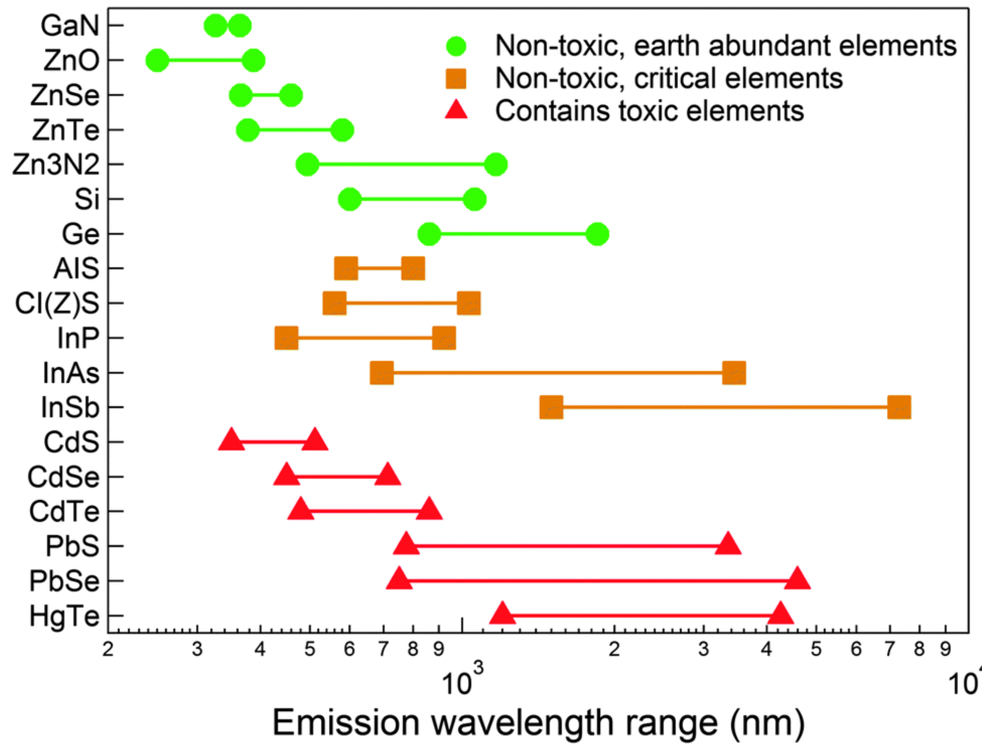
**(1-20nm for quantum dots)**

# Low cost through the hot injection synthesis



# Spectral tunability through quantum confinement effect

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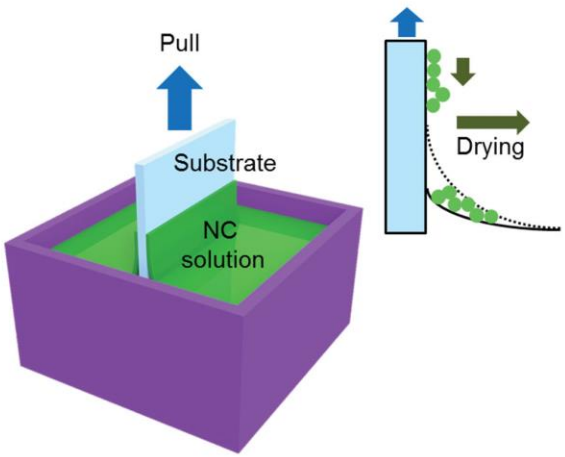
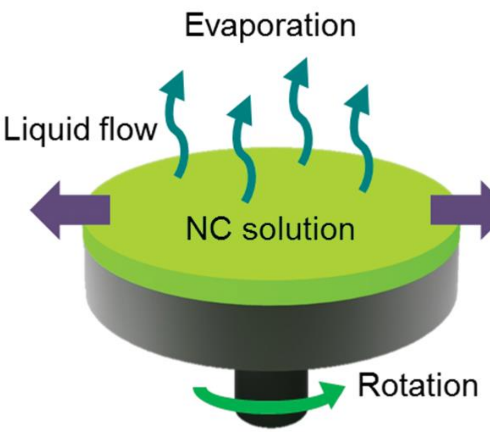
# EASY HETEROGENEOUS INTEGRATION ON SI/SOI

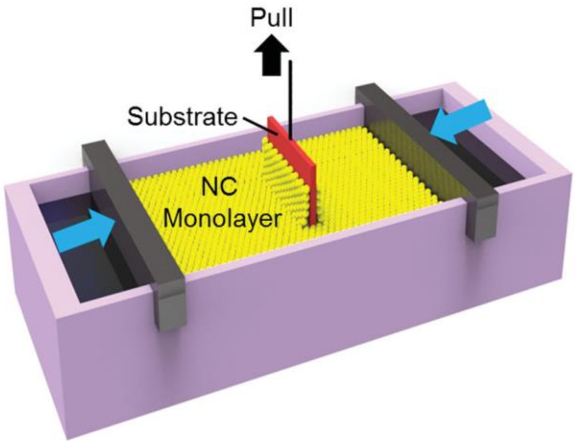
- Dip coating



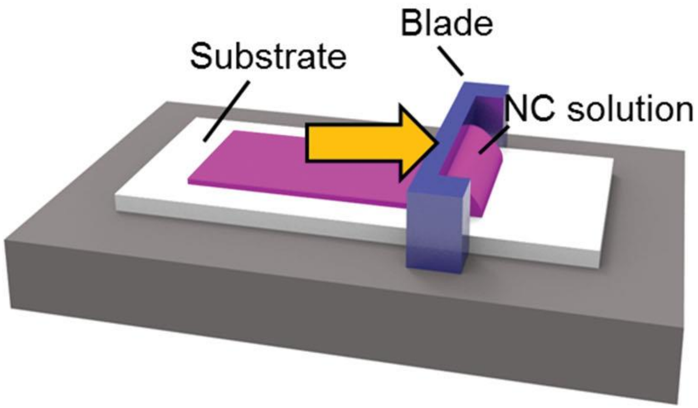

- Spin coating




- Langmuir-Blodgett deposition

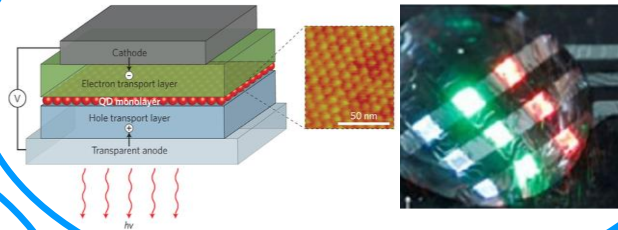



- Doctor blading

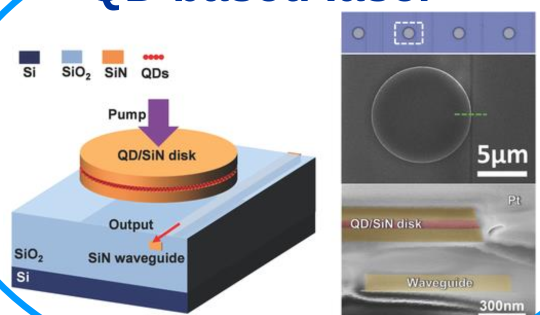


# APPLICATIONS BASED ON COLLOIDAL QUANTUM DOTS

## Light emitting diodes

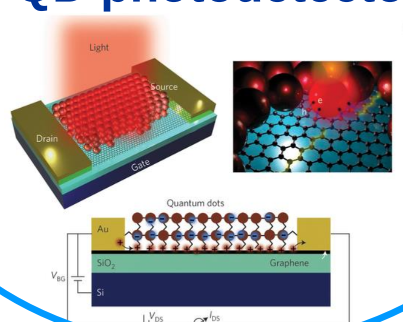



## QD based laser




## QD display


## QD photodetectors




## Photovoltaics

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- Introduction
- SWIR/MWIR colloidal quantum dot photodetectors
- Measurement results
- Conclusion and future work

# OUTLINE

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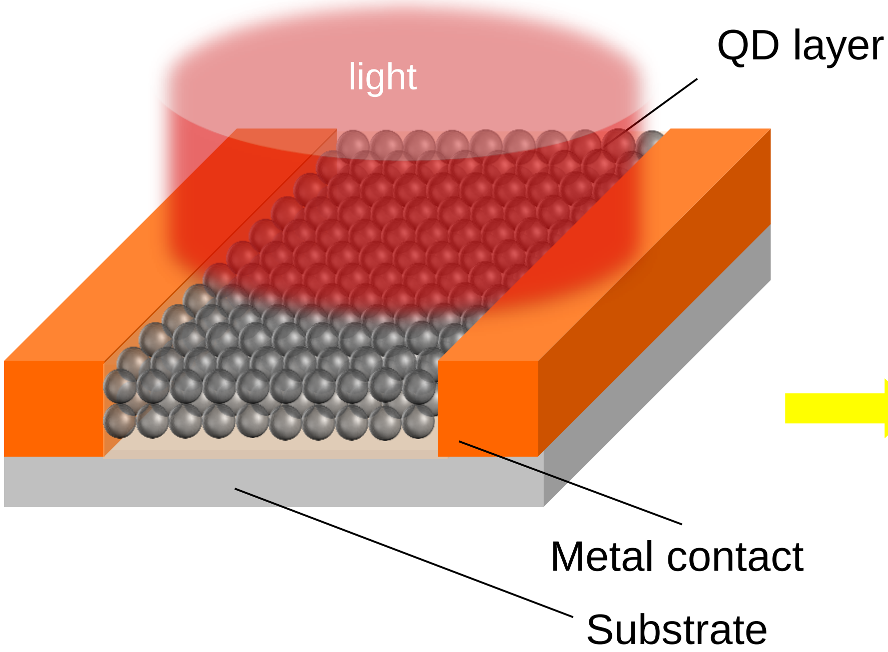
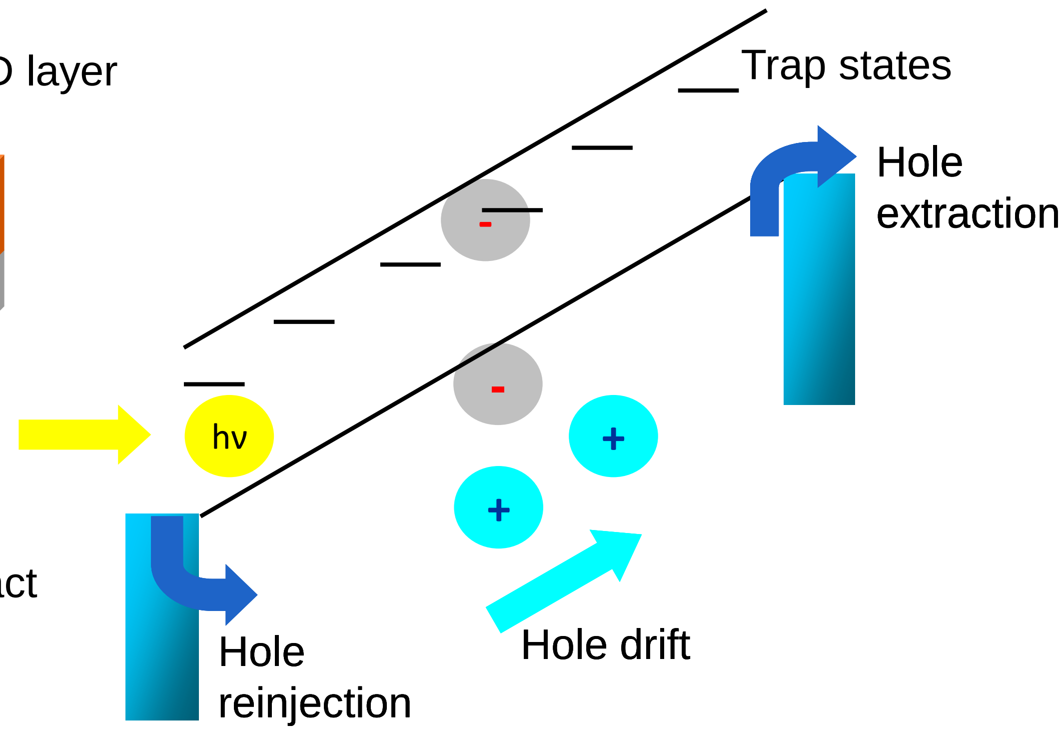
# How to realize photodetection?

## Integrated MIR QD Photodetectors




## Interband transition




**Gain = carrier lifetime / carrier transit time**

**Filling of trap states reduces responsivity at higher input power**

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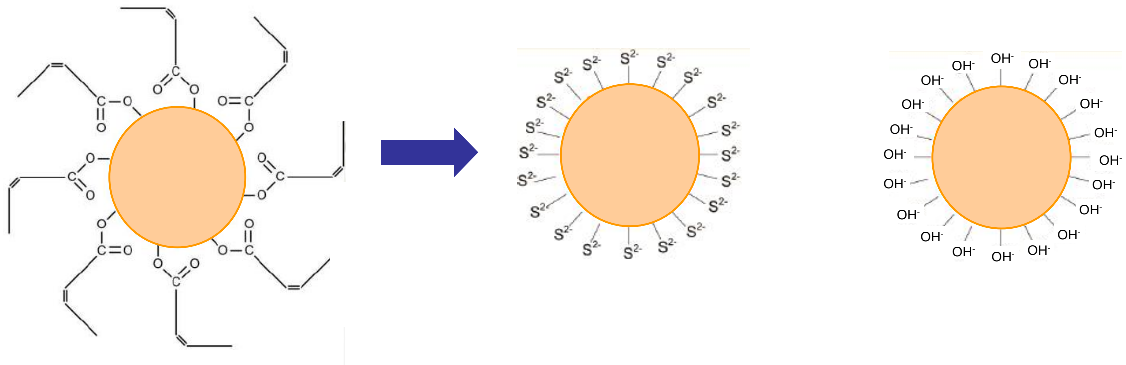
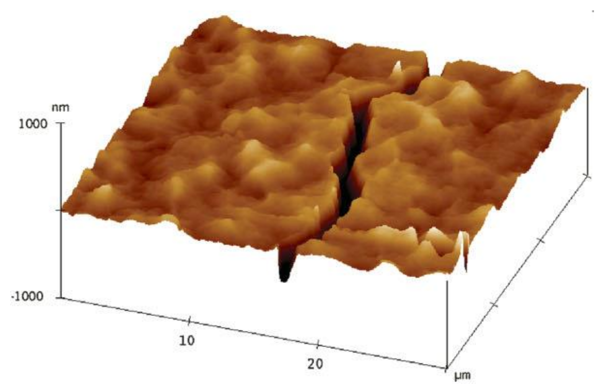
# CHALLENGES OF INTEGRATION?

- **Isolating organics**



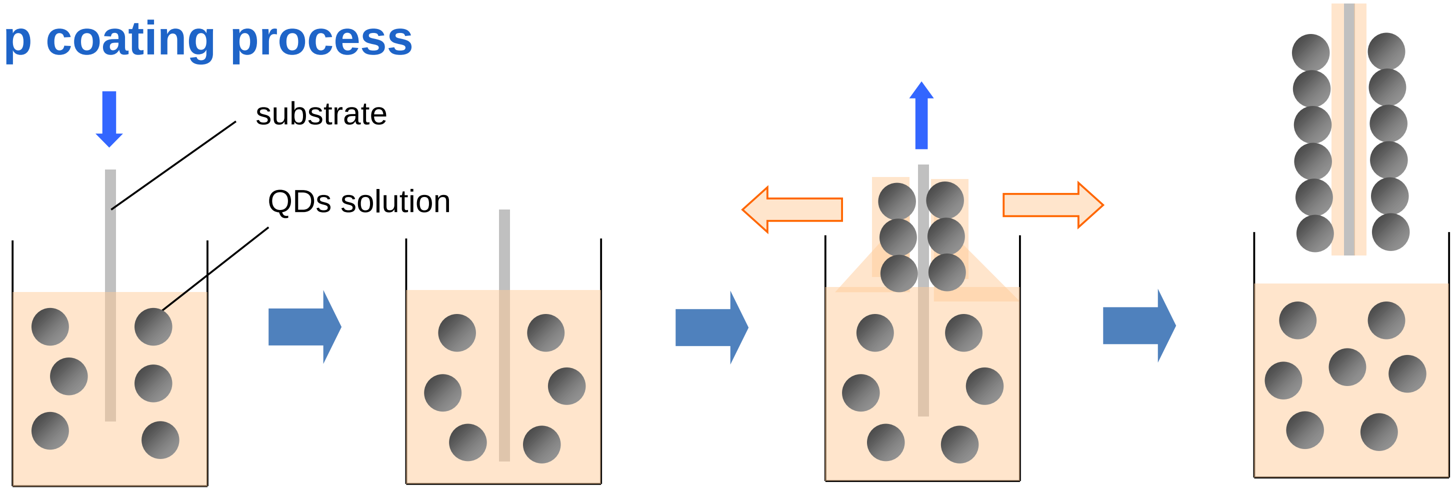
- **Film cracking due to significant volume loss during ligand exchange**

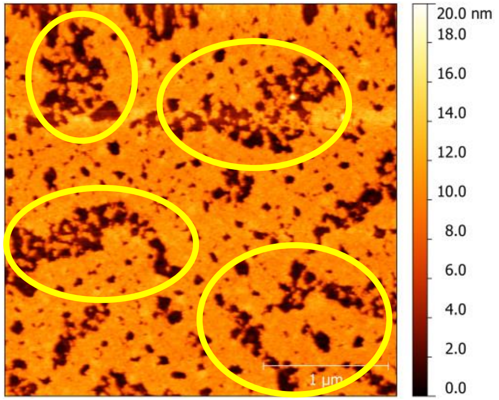
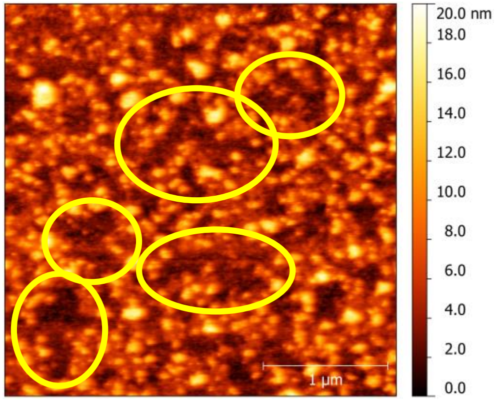
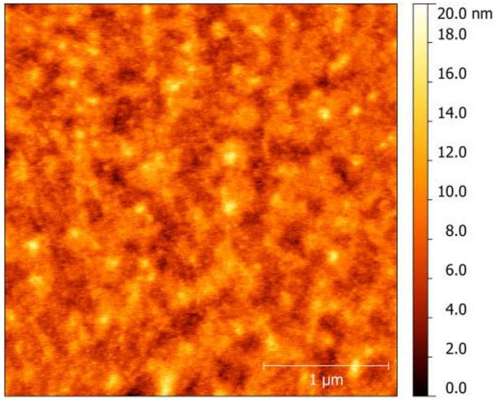



- **Patterning of colloidal QD film**
- **Stability issues (oxidation, etc.)**

# Quantum dot films formed through dip coating

- **Dip coating process**

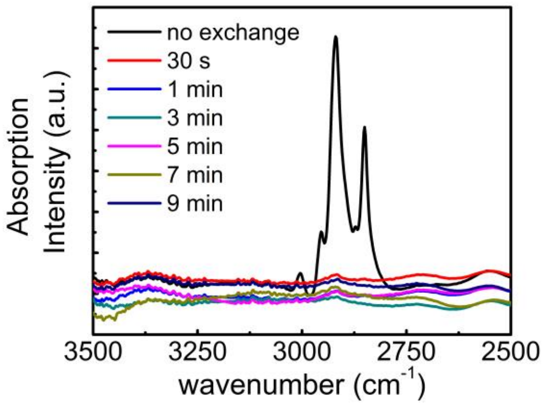



| 80 mm/min withdrawal speed and 100 nM concentration | 20 mm/min withdrawal speed and 1 µM concentration | 80 mm/min withdrawal speed and 1 µM concentration |
|---|---|---|
|  |  |  |

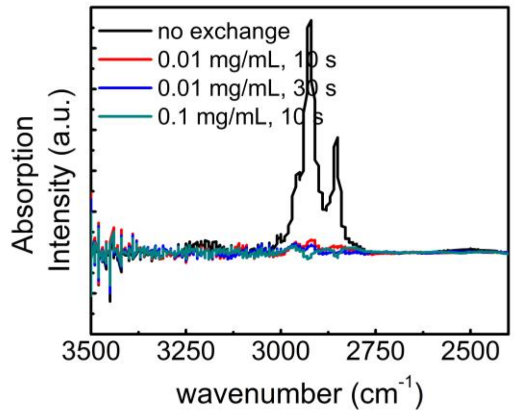
# INORGANIC LIGAND EXCHANGE

## FTIR measurement:

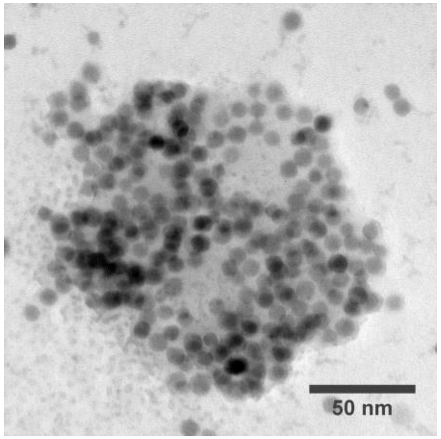
### $S^{2-}$ ligand exchange




### $OH^-$ ligand exchange

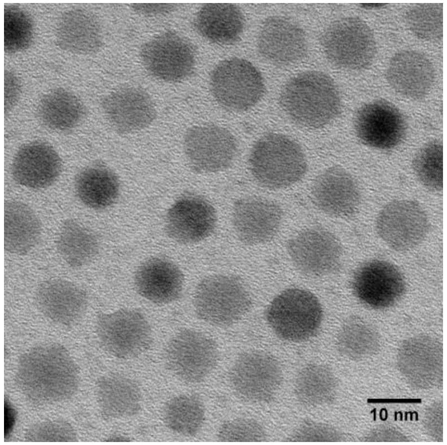



### A thorough cleaning is also needed

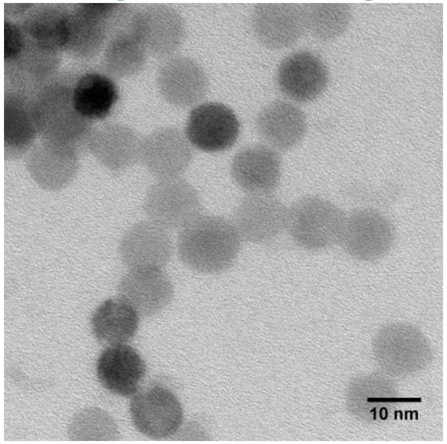



## TEM measurement:

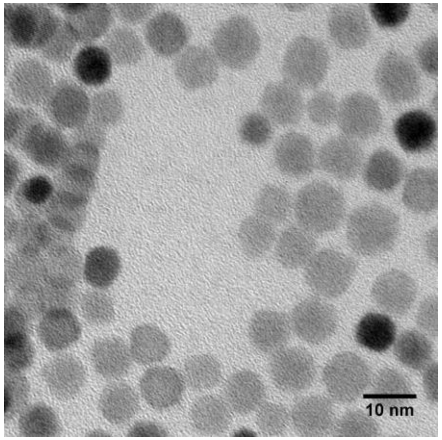
### PbS-OlAc QDs




### $S^{2-}$ ligand exchange




### $OH^-$ ligand exchange

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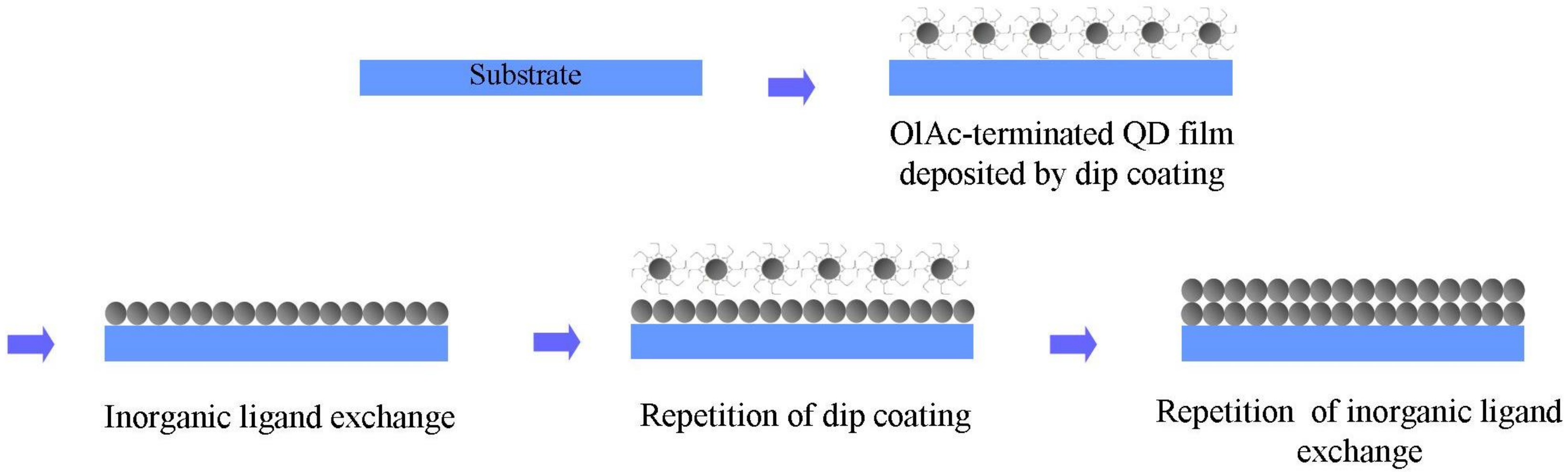
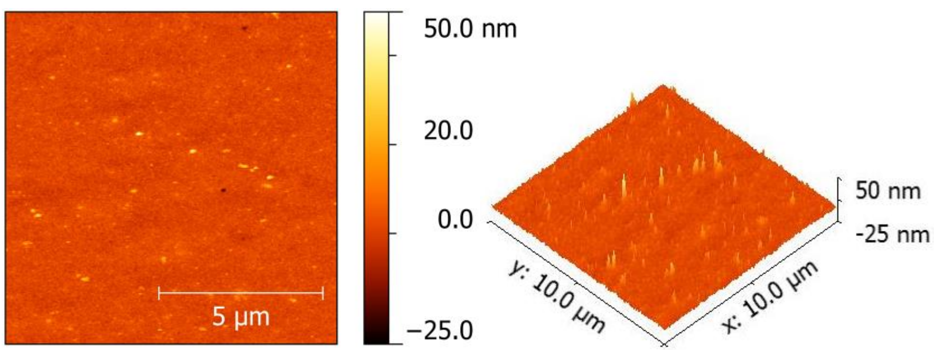
# LAYER-BY-LAYER ASSEMBLY METHOD

## Process flow:

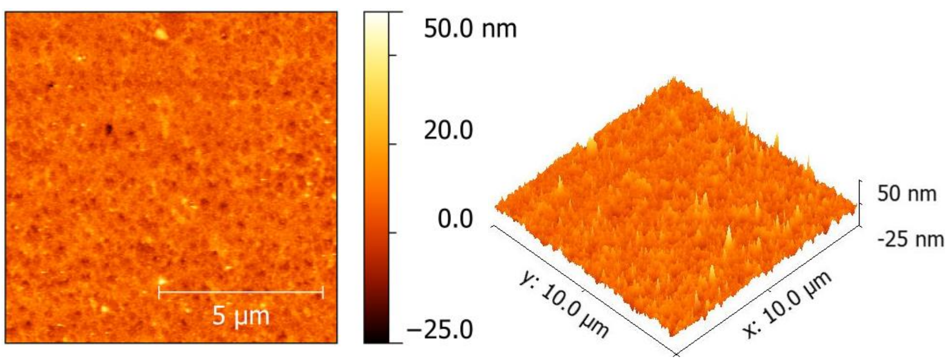



## PbS/$S^{2-}$ QD film




RMS Roughness ~ 5.5 nm

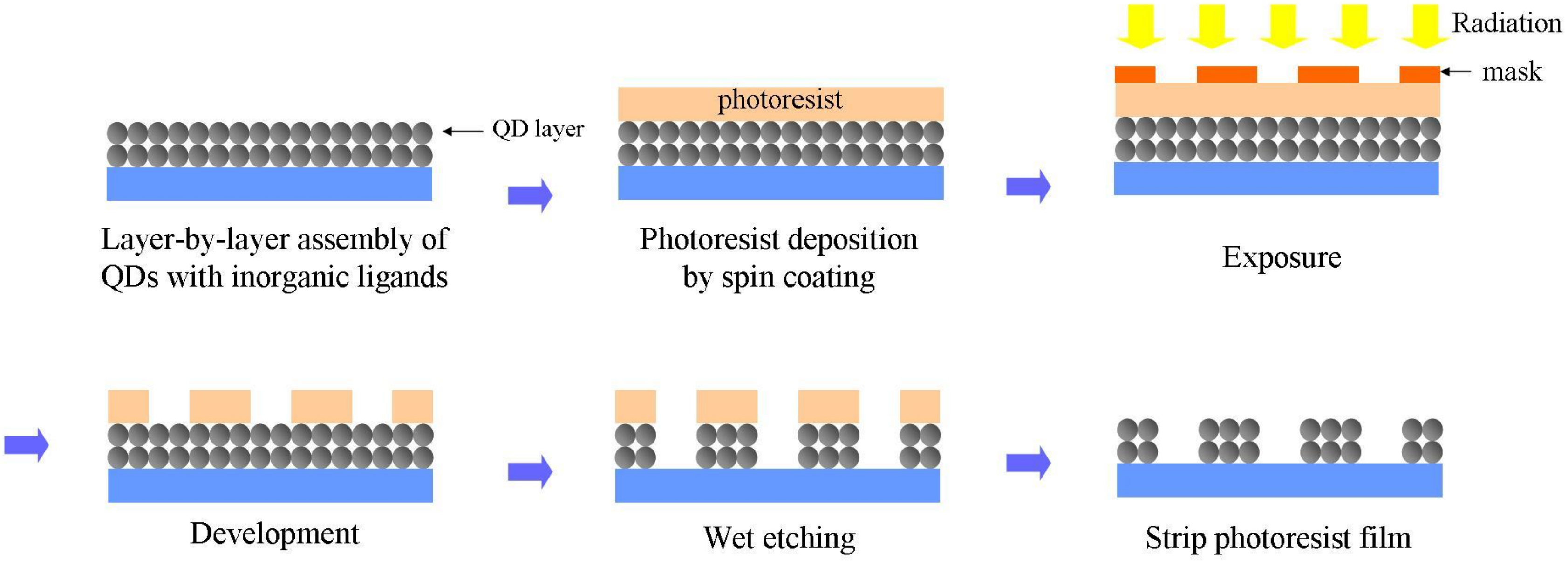
## PbS/$OH^-$ QD film




RMS Roughness ~ 4.5 nm

# PATTERNING OF NANOCRYSTAL FILM BY WET ETCHING

## Process flow:




C. Hu, *et al.* “The micropatterning of layers of colloidal quantum dots with inorganic ligands using selective wet etching” *Nanotechnology* ***2014***

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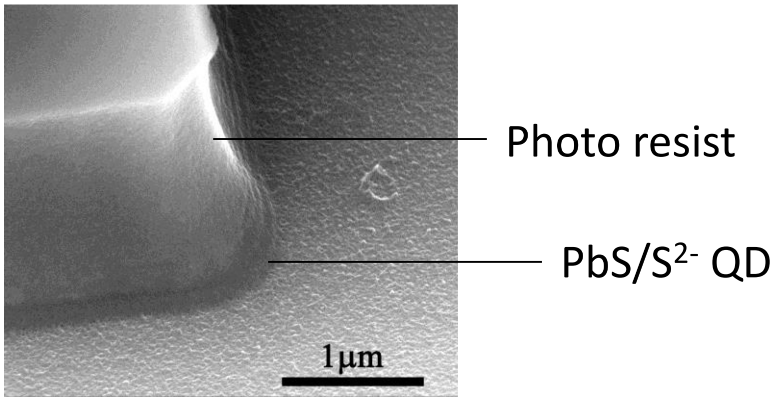
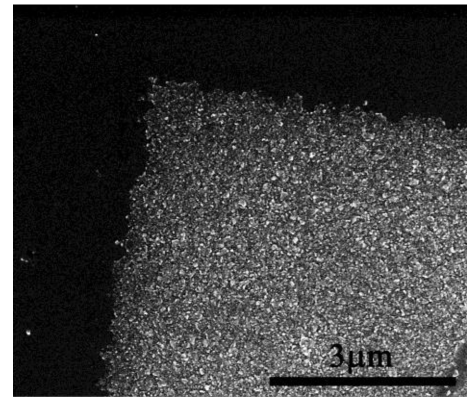
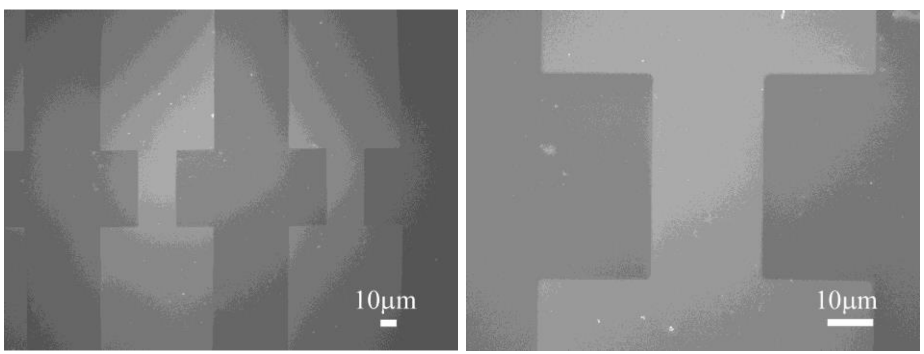
# MICROPATTERNING OF PBS NANOCRYSTAL FILM ON 2D SUBSTRATES

$HCl/H_3PO_4$ mixture with 1:10 volume ratio

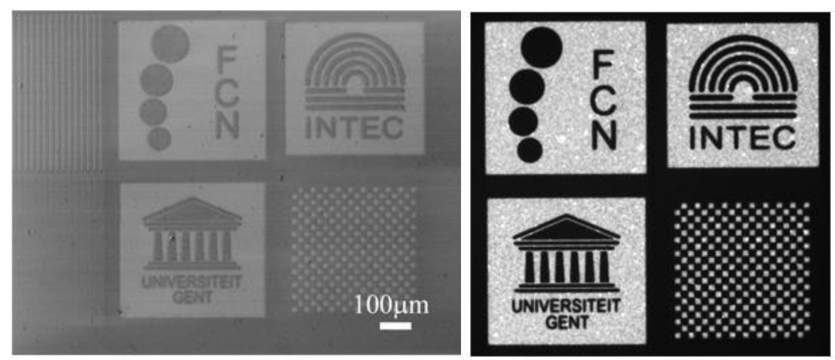



**$PbS/S^{2-}$ QD film**




**CdSe/CdS QD film**

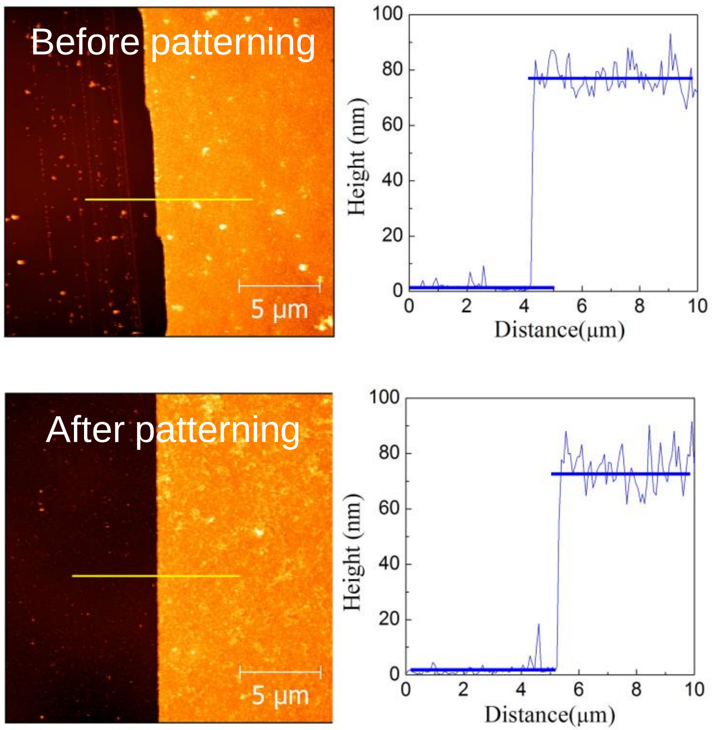



The etching rate for $PbS/S^{2-}$ and $PbS/OH^-$ films is ~ 40 nm/min and 45 nm/min, respectively

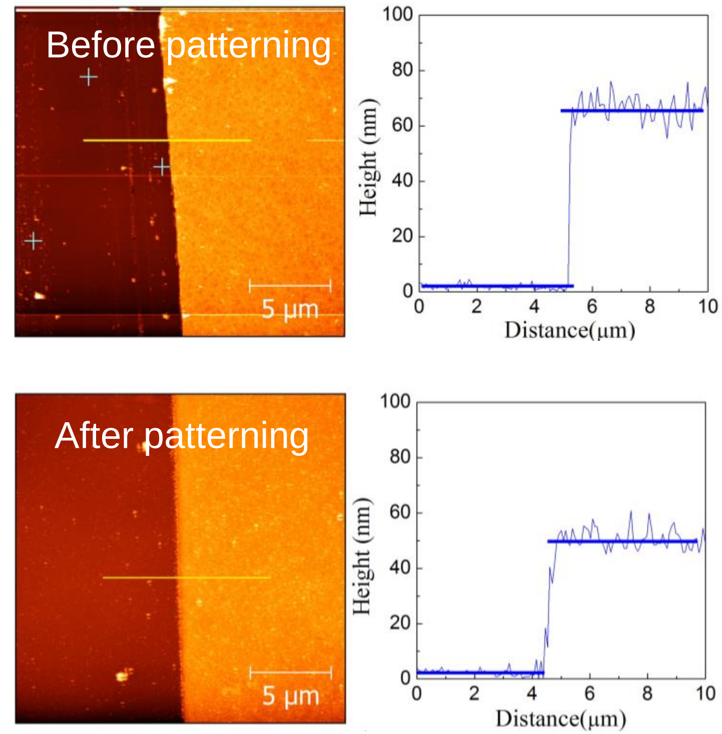
# MICROPATTERNING OF PBS NANOCRYSTAL FILM ON 2D SUBSTRATES

Any effect of lithography/patterning on original morphology of the film?

**PbS/$S^{2-}$ QD film**




**PbS/$OH^{-}$ QD film**




Effect by lithography/patterning is not obvious and can be neglected!

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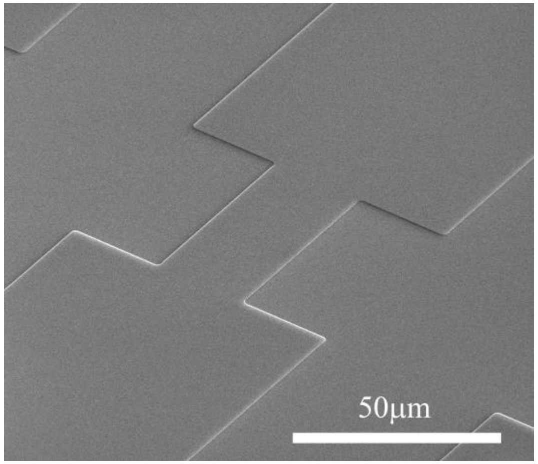
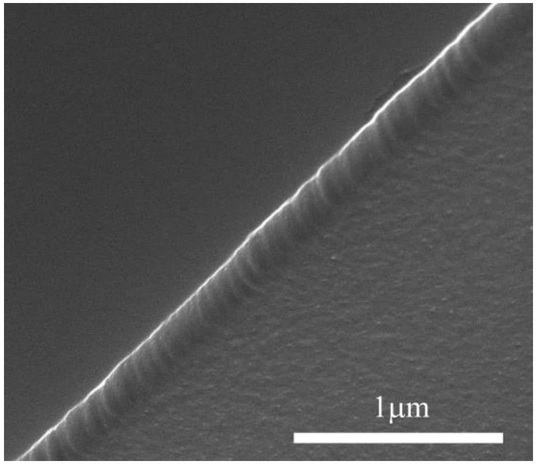
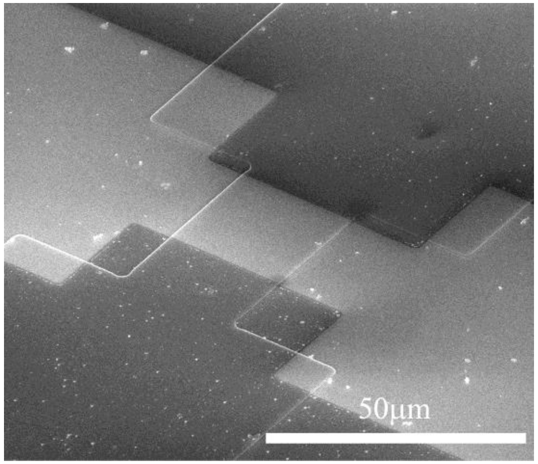
# Micropatterning of PbS nanocrystal film on 3D substrates

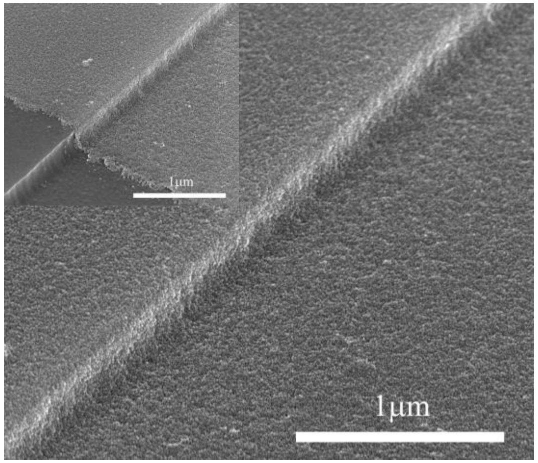
## SEM measurement of 3D Si substrates:

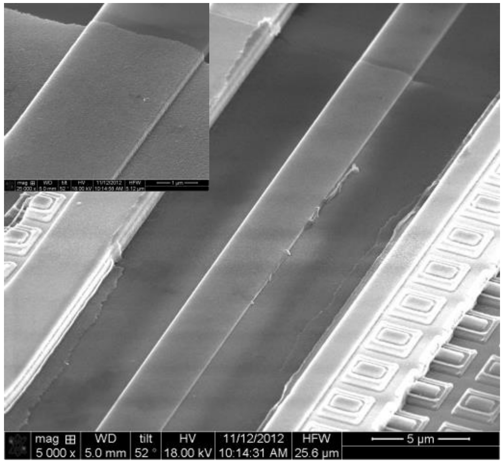



## Micropatterned PbS/OH$^-$ films on 3D Si substrates and waveguides

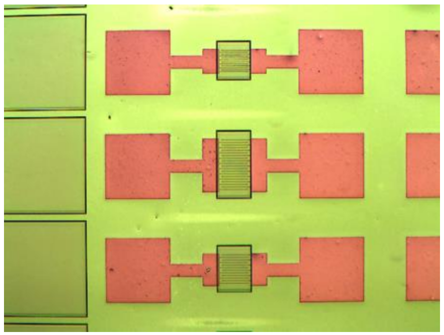


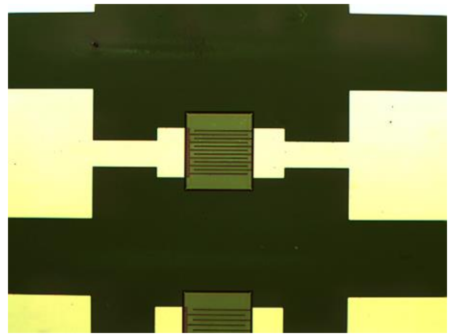



# PATTERNING OF PBS NANOCRYSTAL FILM ON PHOTODETECTOR

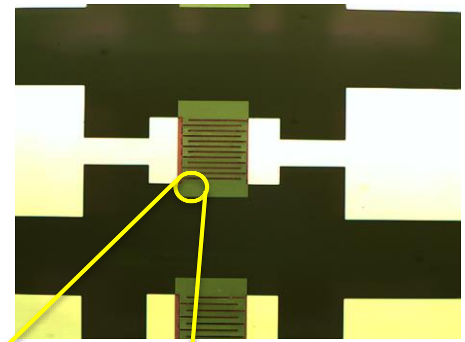
Before etching

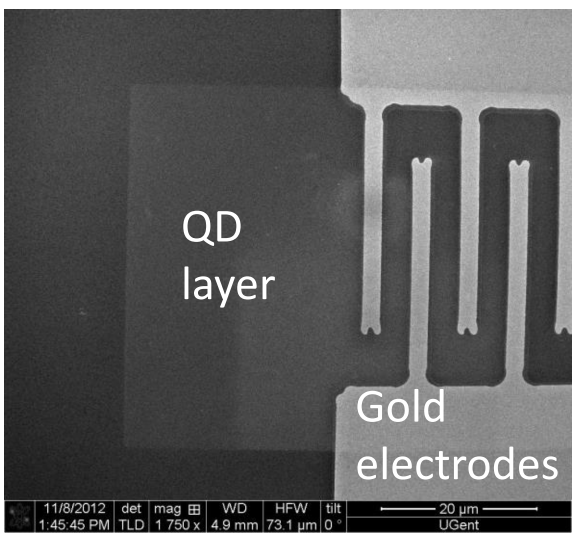


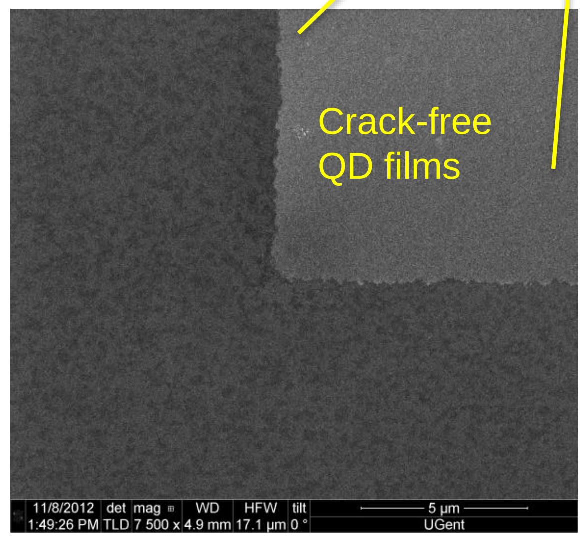
Before removing resist



After removing resist





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# OUTLINE

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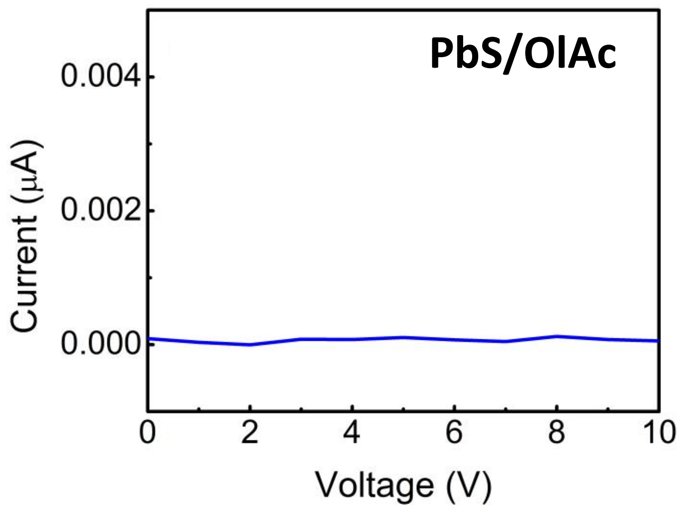
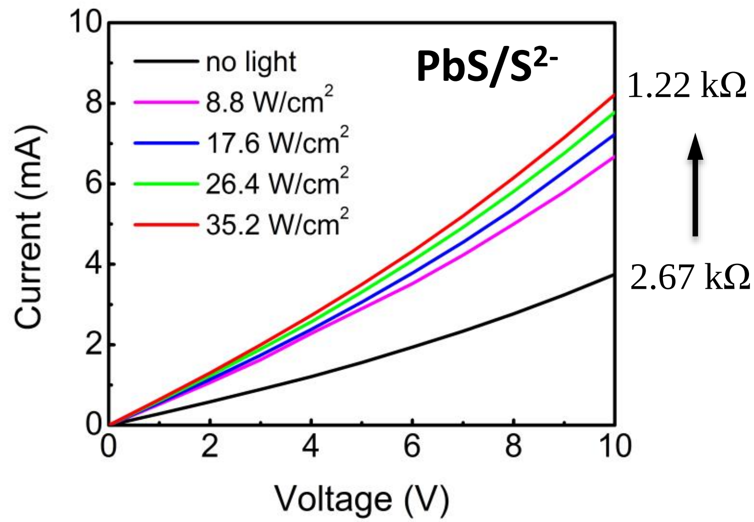
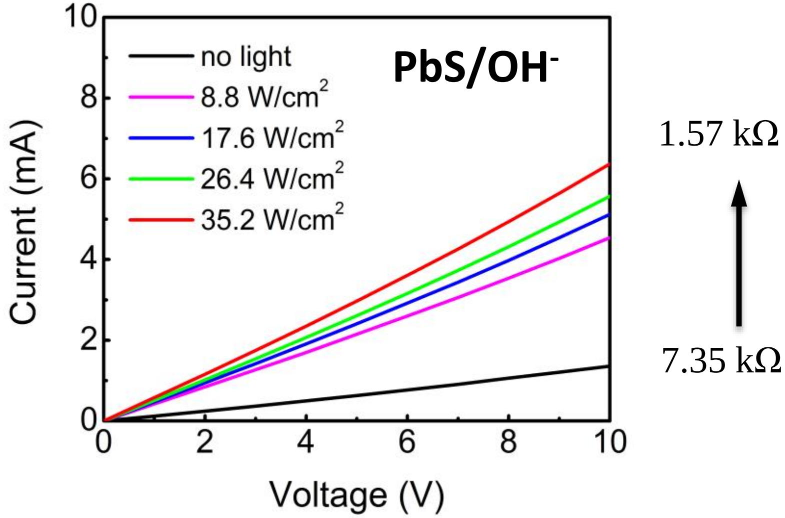
# CHARACTERIZATION OF PBS QD PHOTODETECTOR



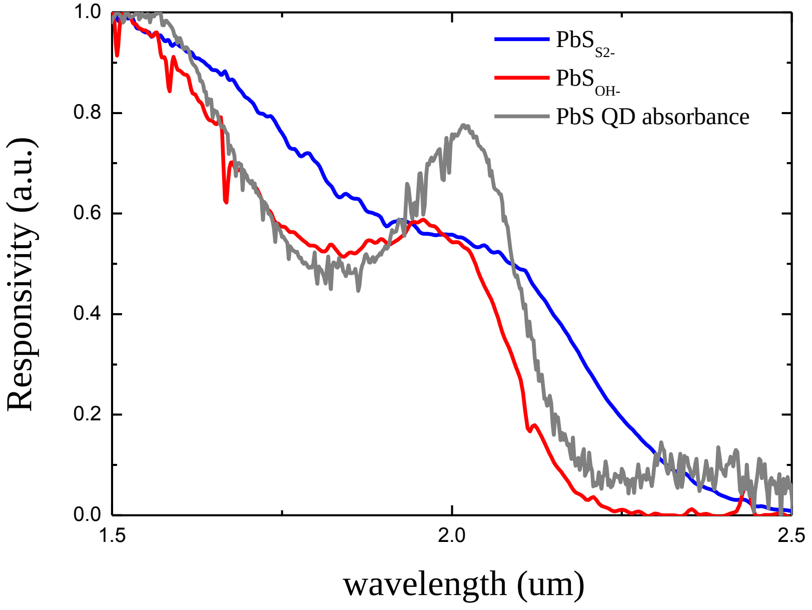




After ligand exchange, the QD films exhibit linear photoconductive property with Au electric contact without Coulomb blockade phenomena

**C. Hu, *et al.* PhotWest 2012**

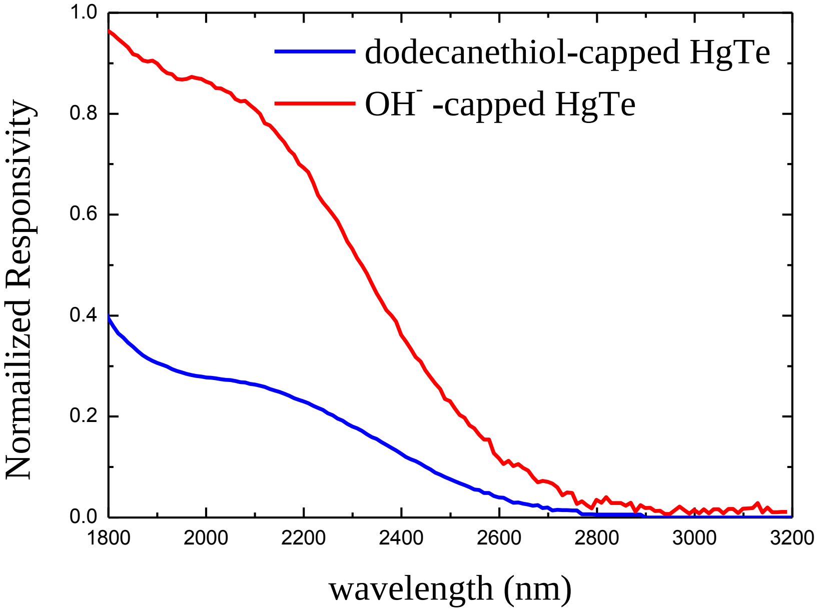
# DETECTOR CHARACTERIZATION WITH FTIR

## PbS QD photodetector




Spectral response curves nearly match the quantum-confined absorption spectrum

## HgTe Photodetector: pushing the cut-off wavelength




With $OH^-$ ligand exchange, the HgTe QD photodetector has 3 time higher responsivity than dodecanethiol-capped QDs.

**Collaboration with Univ Linz**

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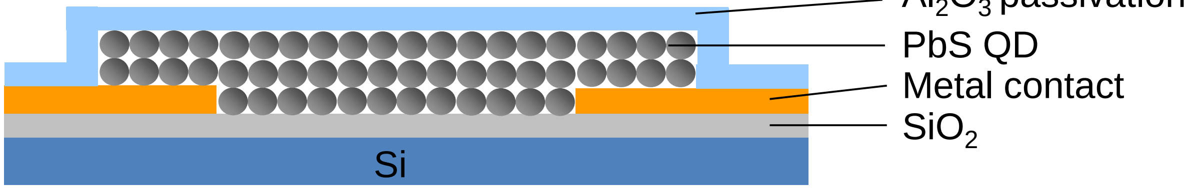
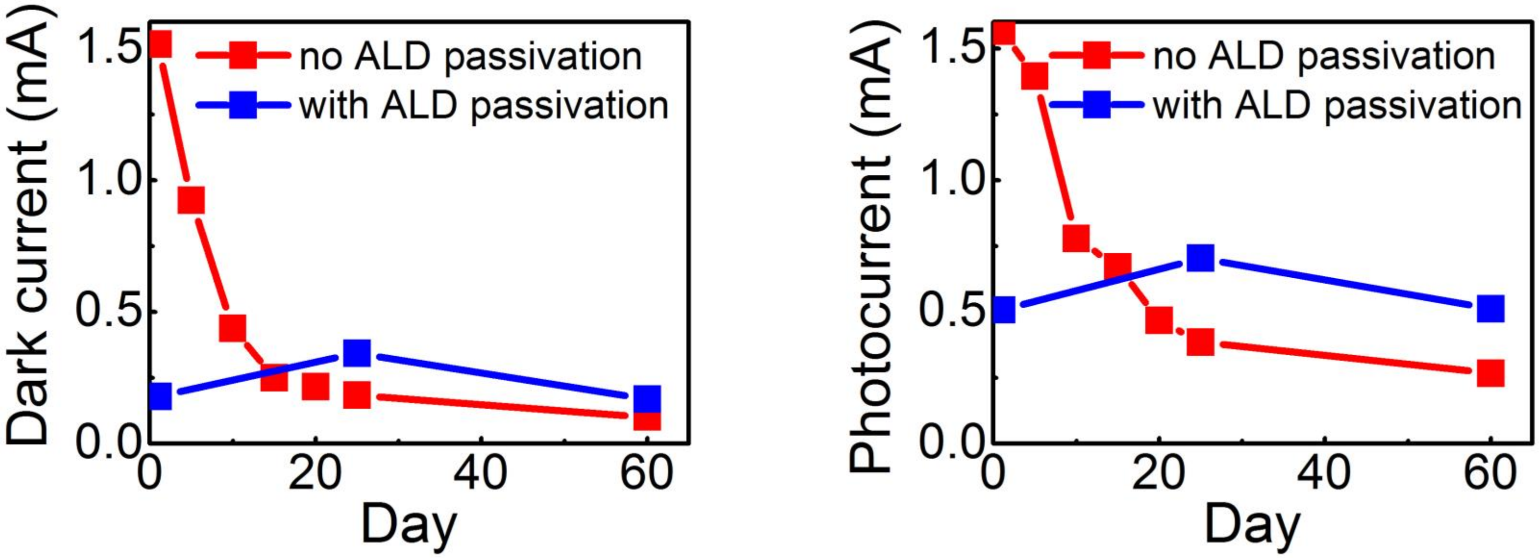
# PASSIVATION WITH ATOMIC LAYER DEPOSITION (ALD)

## Problem: Degradation of the photodetector due to oxidization

ALD: $Al_2O_3$ ~ 30 nm



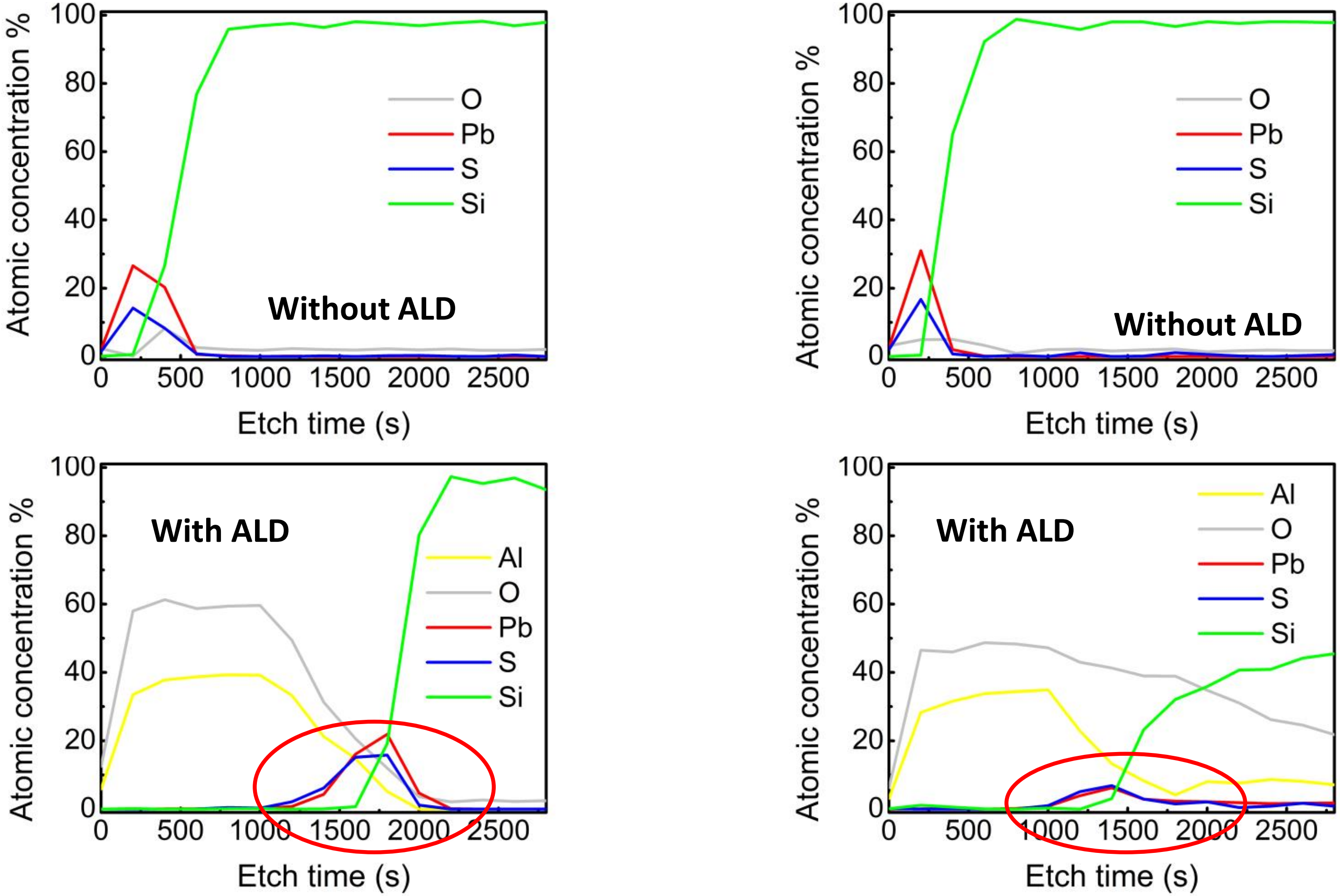

**PbS/$S^{2-}$ QD detector (15 LBL)**



# CHARACTERIZATION ON ALD COATED PBS QD FILM

## X-ray photoelectron spectroscopy measurement

**PbS/$S^{2-}$ QD film** | **PbS/$OH^{-}$ QD film**

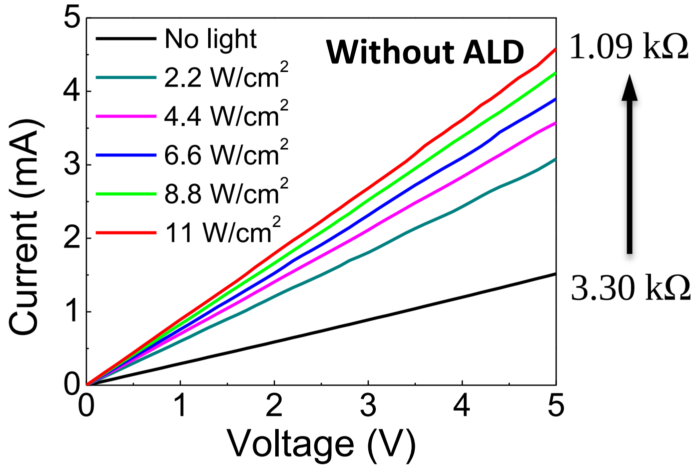


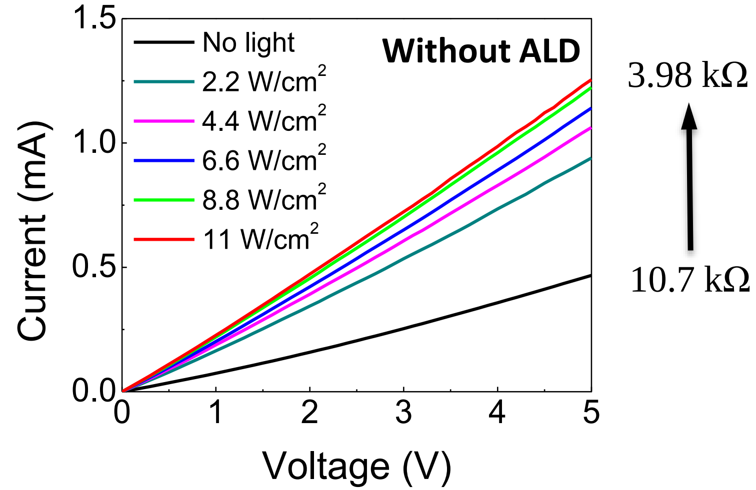

After direct ALD passivation, both dark current/photocurrent are quenched, this can be attributed to alumina penetration during ALD process

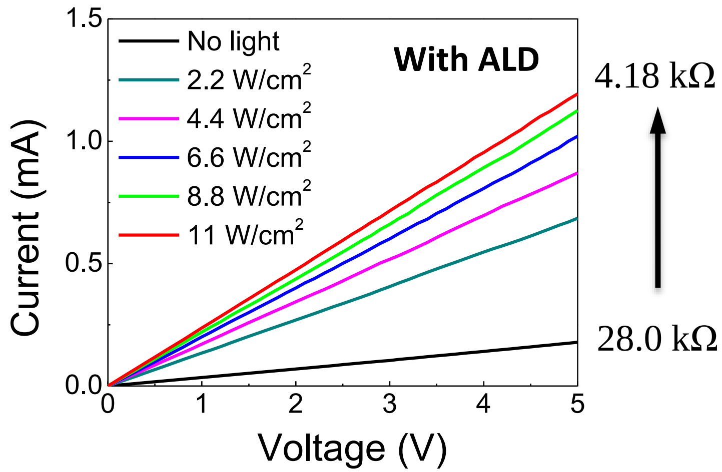
# CHARACTERIZATION OF PBS QD-ALD PHOTODETECTOR (I)

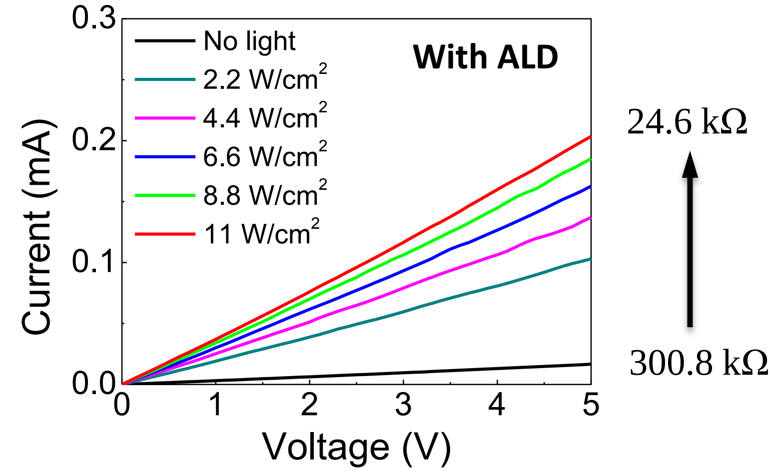
## PbS/$S^{2-}$ QD photodetector

## PbS/$OH^-$ QD photodetector

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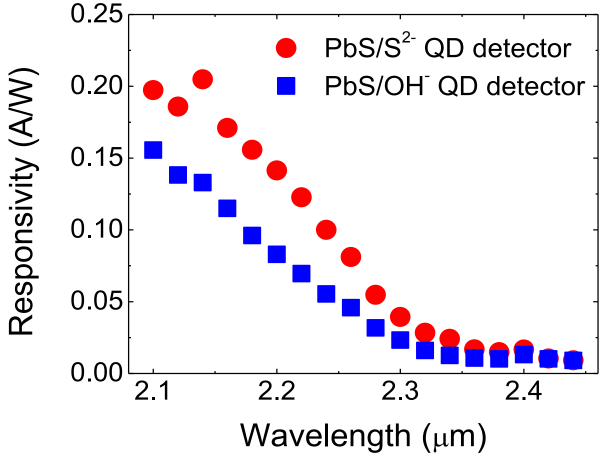
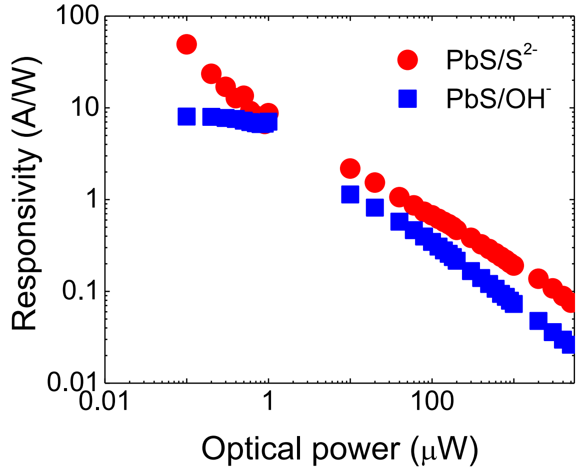
# CHARACTERIZATION OF PBS QD-ALD PHOTODETECTOR (II)

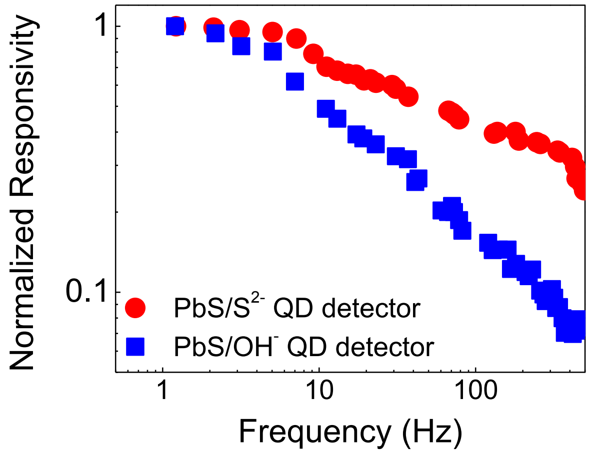
## Spectral Response




## Responsivity vs. Optical Illumination




## Electrical Frequency Response




The corresponding specific detectivity is ~ $3.4 \times 10^8$ Jones at 300K.

The 3-dB bandwidth of the $PbS/S^{2-}$ and $PbS/OH^-$ photodetectors is 40 Hz and 11 Hz, respectively.

**C. Hu, *et al.* *Applied Physics Letters* 2014**

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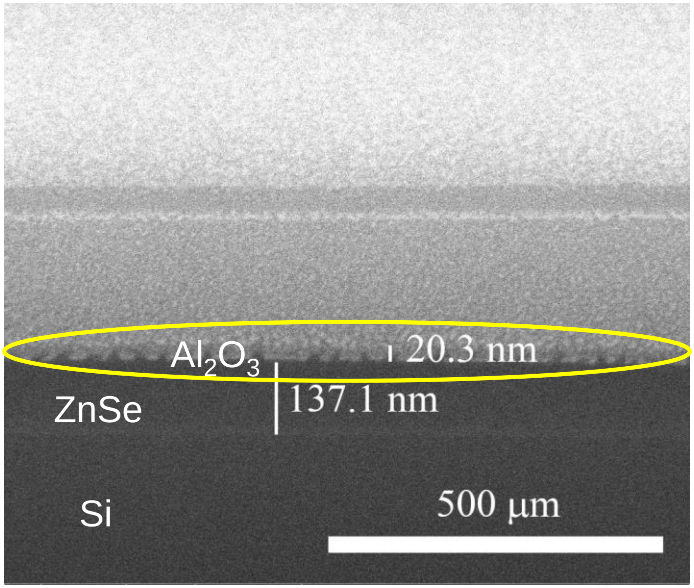
# CAN WE IMPROVE PHOTOCURRENT QUENCHING DURING ALD?

## A sacrificial layer with large band gap material before ALD

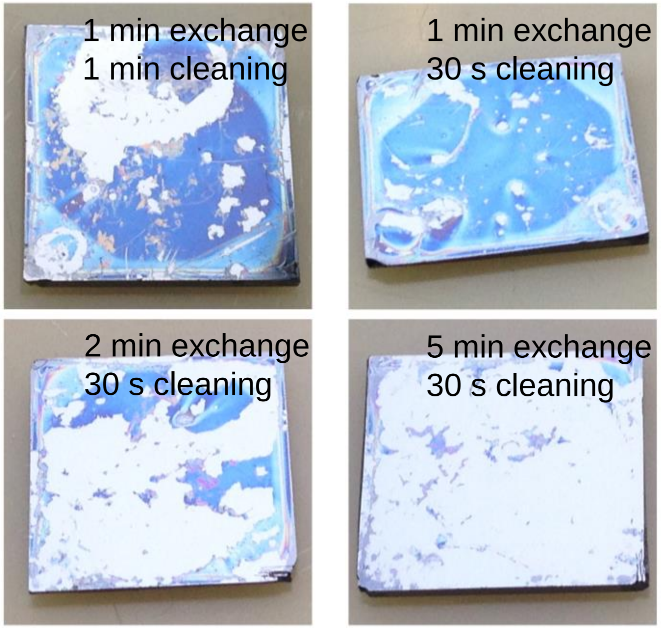
### Route 1: ZnSe QD film as sacrificial layer

**Without $S^{2-}$ exchange**




Without ligand exchange, ZnSe film is not compatible with ALD growth

**With $S^{2-}$ exchange**




ZnSe QD film peeled off during ligand exchange procedure.

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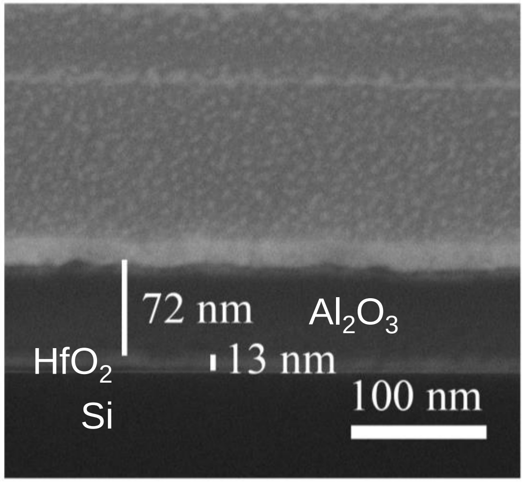
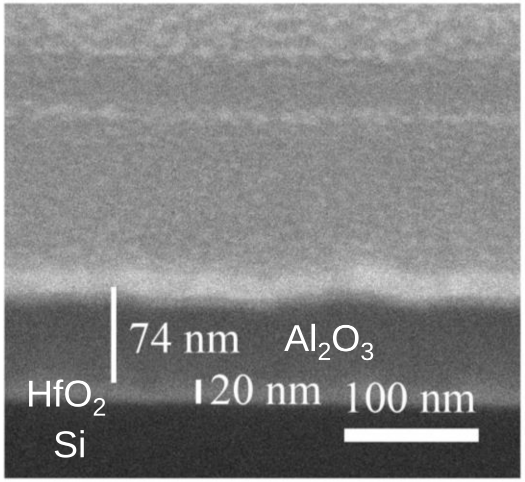
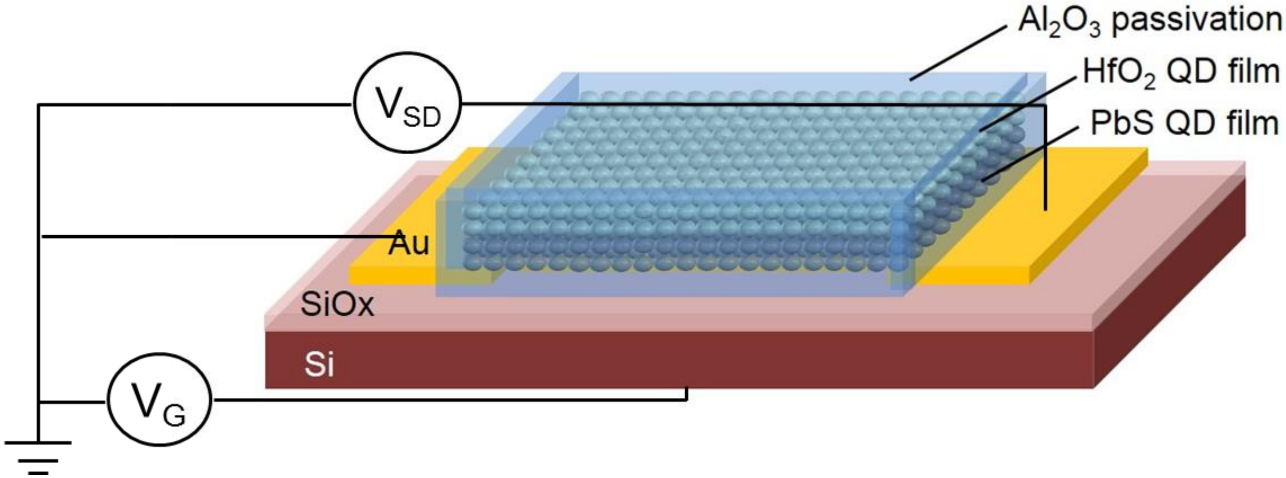
# CAN WE IMPROVE PHOTOCURRENT QUENCHING DURING ALD?

## Route 2: $HfO_2$-$S^{2-}$ QD film as sacrificial layer exhibits ALD compatibility

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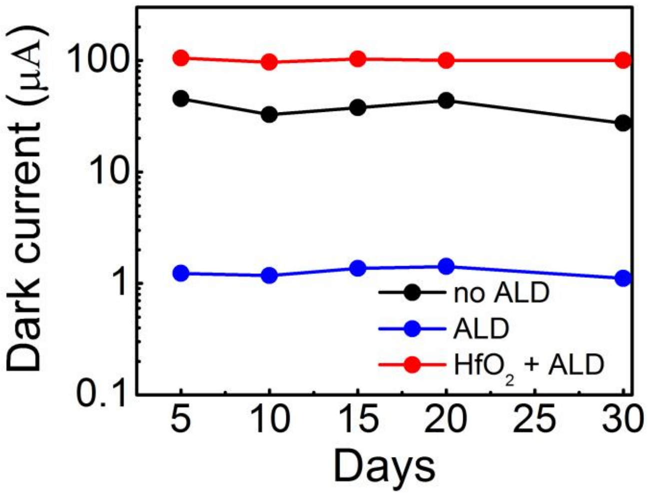
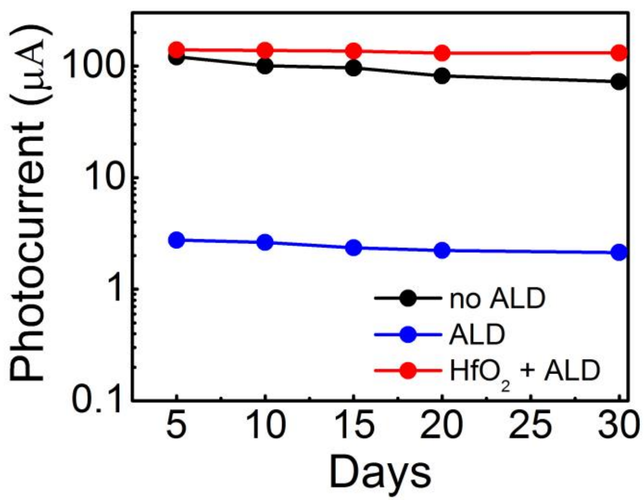
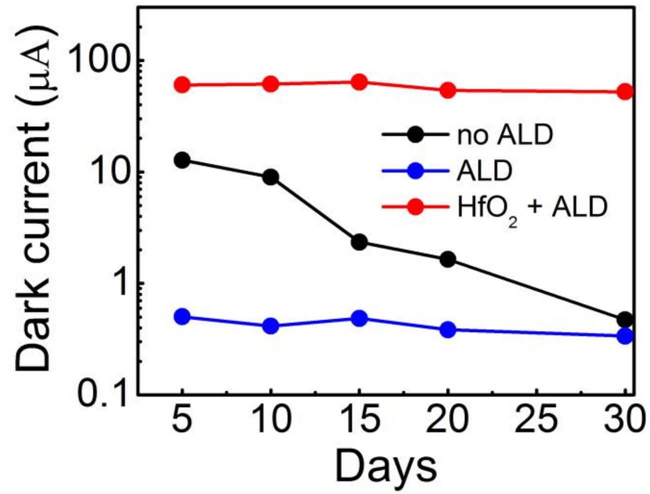
# PbS phototransistor with $HfO_2$ sacrificial layer

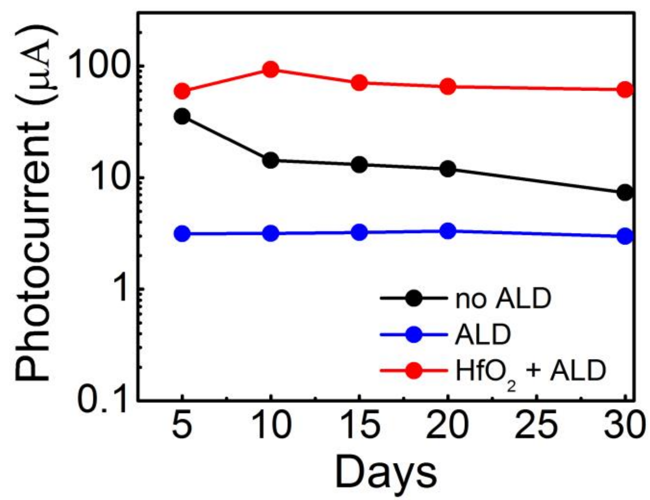
## PbS-$S^{2-}$/$HfO_2$-$S^{2-}$ QD detector (15 LBL)



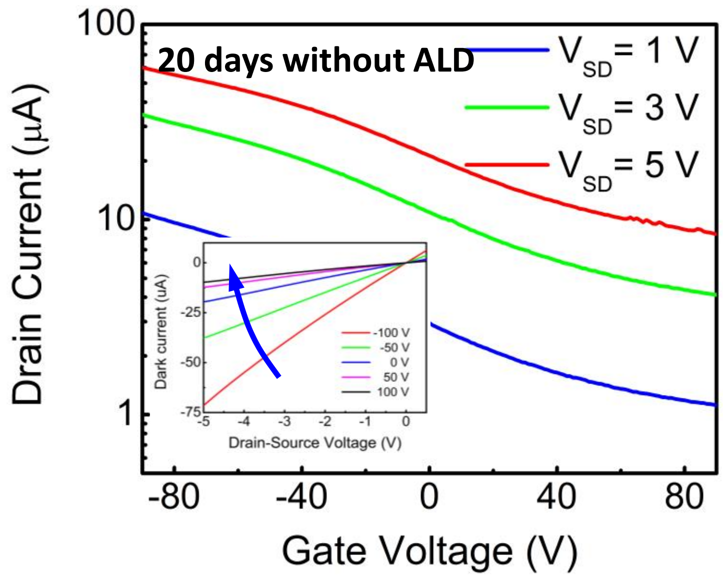



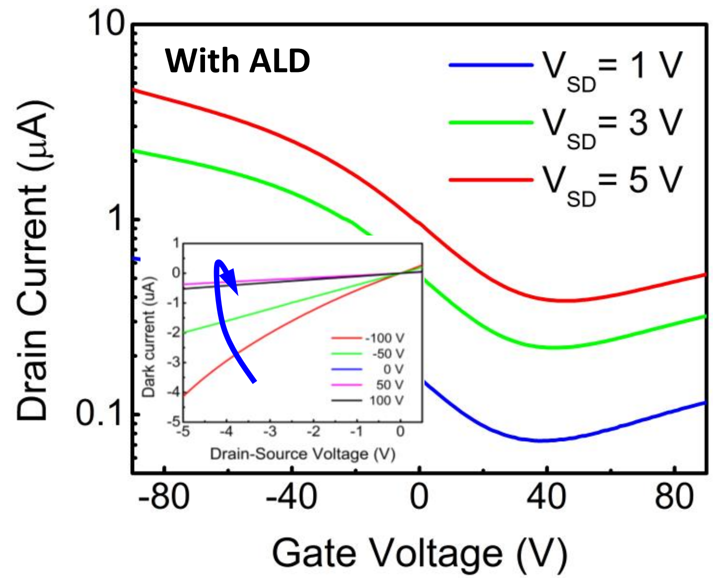

## PbS-$OH^{-}$/$HfO_2$-$S^{2-}$ QD detector (15 LBL)

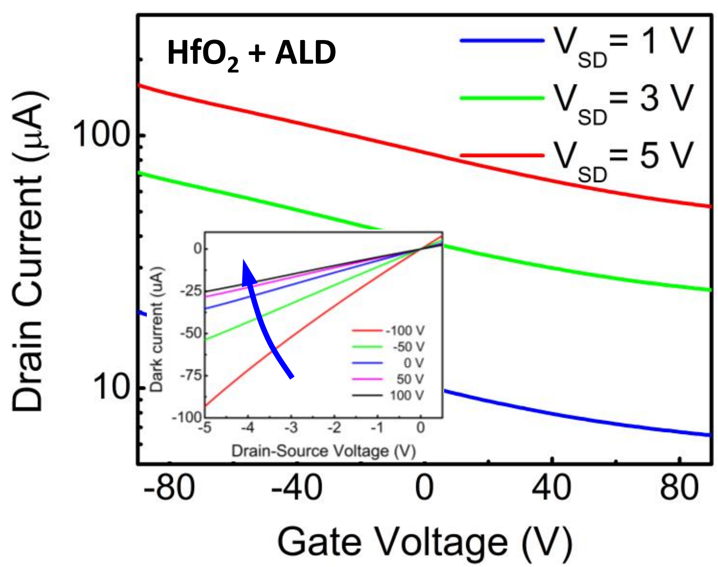


# PHOTOTRANSISTOR MEASUREMENT: PBS/$S^{2-}$ QD

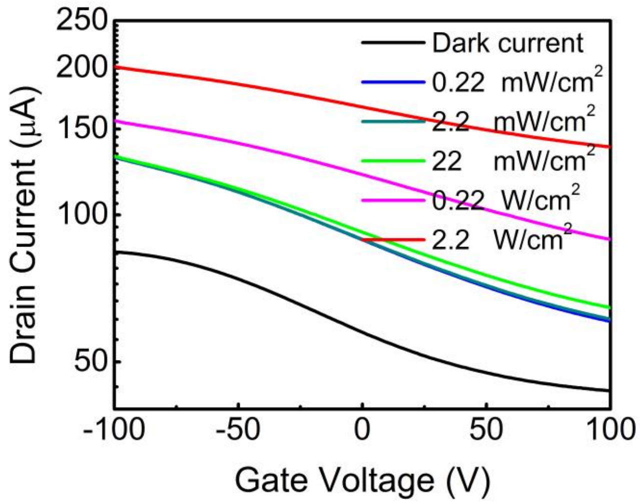


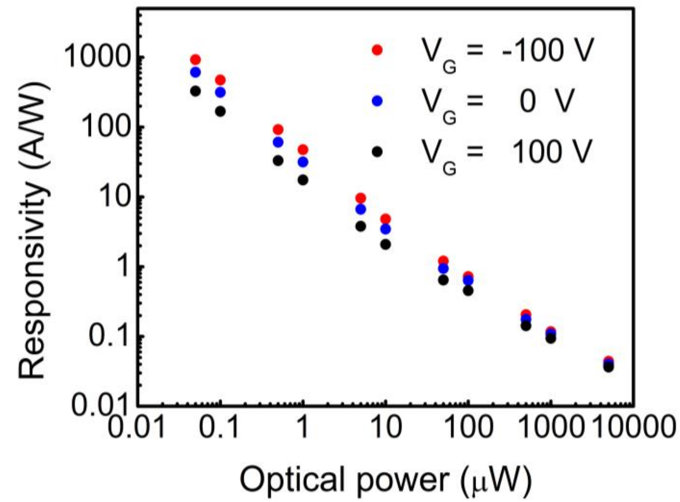



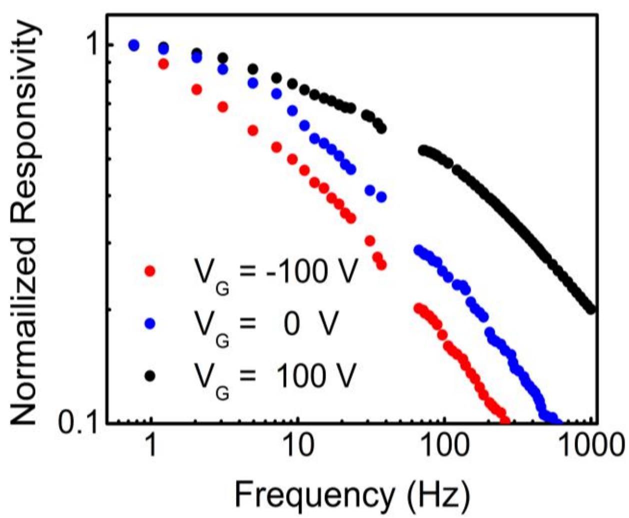




- $S^{2-}$ terminated PbS QD transistors behave as p-type,
- Quasi-linear $I_{SD}$-$V_D$ curves without saturation of $I_{SD}$ , suggesting large hole densities in the FET channel and can not easily be modulated by gate voltage
- After ALD passivation, PbS-$S^{2-}$ QD transistors behave as ambipolar
- With $HfO_2$ sacrificial layer, device exhibit p-type again, Calculated holes linear mobility $\mu_{lin}$ ~ 0.025 $cm^2/(V\cdot s)$ @ 5V

# CHARACTERIZATION OF $PbS/S^{2-}$ PHOTOTRANSISTOR




- At 5 V Drain bias, 110 μW/cm$^2$ incident power, responsivity ~ 930 A/W @ -100 V gate voltage for $PbS/S^{2-}$ phototransistor;
- The 3-dB bandwidth @ -100 V and @ 100 V gate voltage of the $PbS/S^{2-}$ phototransistors is 3 Hz and 19 Hz, respectively.

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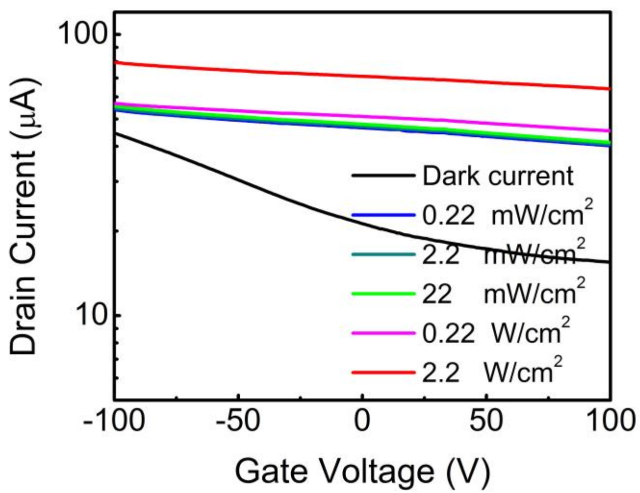
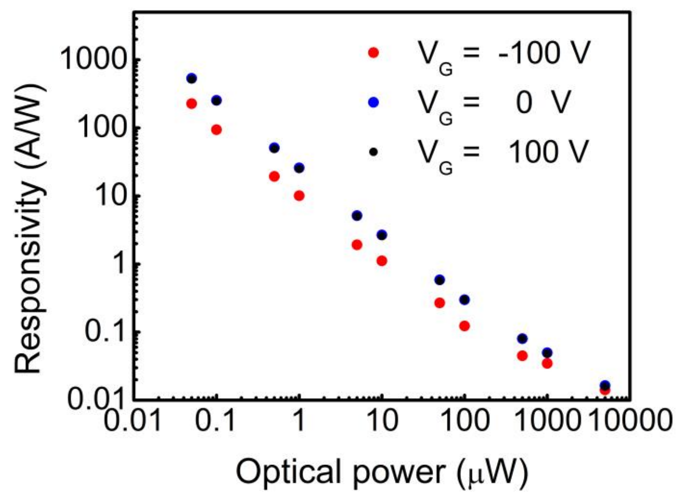
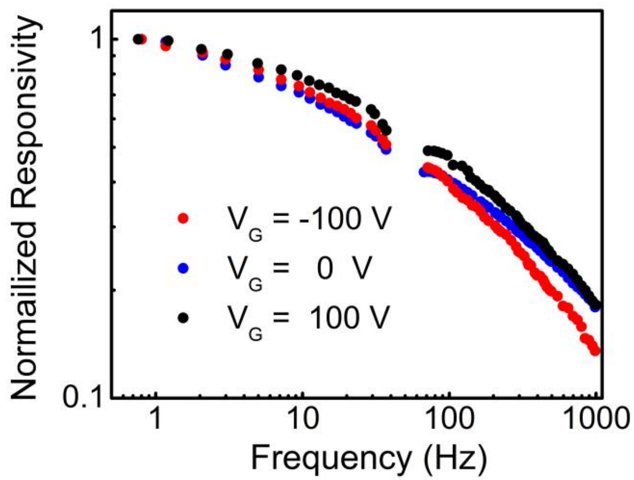
# Characterization of PbS/OH$^-$ Phototransistor




- At 5 V Drain bias, 110 μW/cm$^2$ incident power, responsivity ~ 230 A/W @ -100 V gate voltage for PbS/OH$^-$ phototransistor;

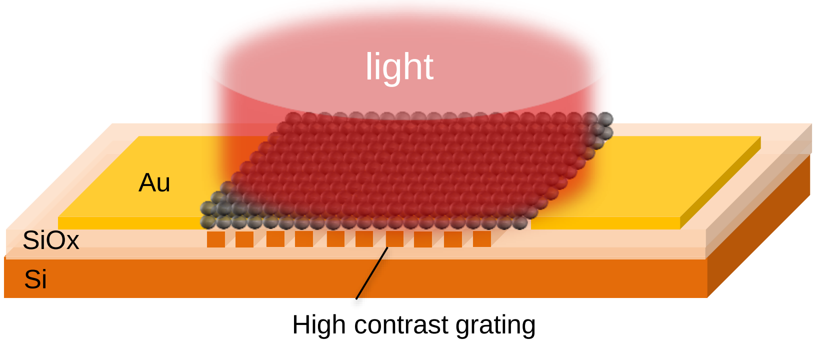
- The 3-dB bandwidth @ -100 V and @ 100 V gate voltage of the PbS/S$^{2-}$ phototransistors is 12 Hz and 17 Hz, respectively.

# CONCLUSION

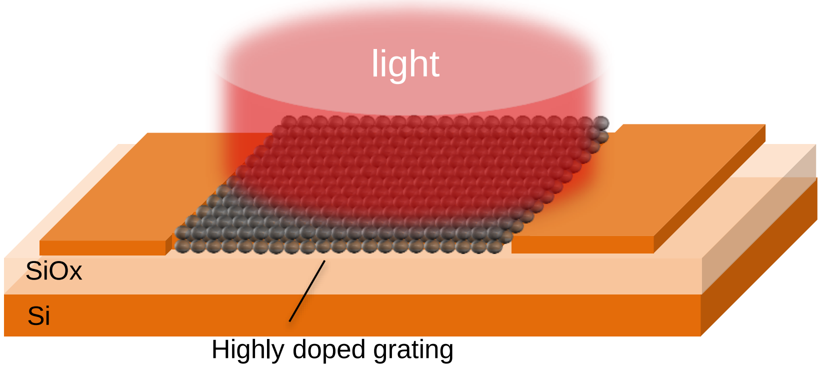
- Crack-free, homogeneous quantum dot films were obtained through a layer-by-layer deposition approach with solid-state ligand exchange
- High resolution colloidal QD films with feature dimensions down to 500 nm can be realized through optical lithography and selective wet etching method for large scale integration applications
- Air-stable PbS colloidal QD photodetectors and phototransistors on Si with high responsivity were obtained

# CAN WE FURTHER ENHANCE THE SENSITIVITY?

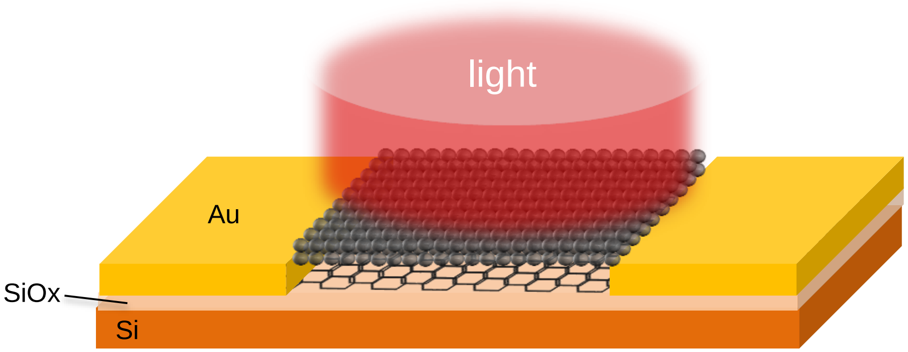
- Increase the absorption of light in the thin film
  $\Rightarrow$ silicon resonant grating structures




- Reduce shadowing from metals
  $\Rightarrow$ doped grating




- Enhance the mobility in the film to enhance the internal gain: QD + graphene or "artificial graphene"



# ACKNOWLEDGEMENT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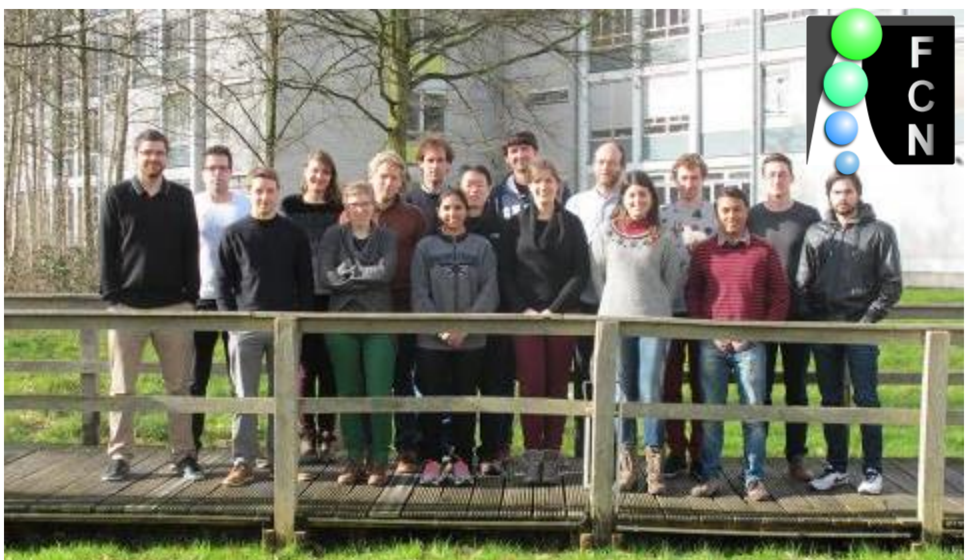
Ghent University

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## Thank you very much for your attention!



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