# Optoelectronic Characterization and Device Considerations of Next-generation Solution-processed Semiconductors

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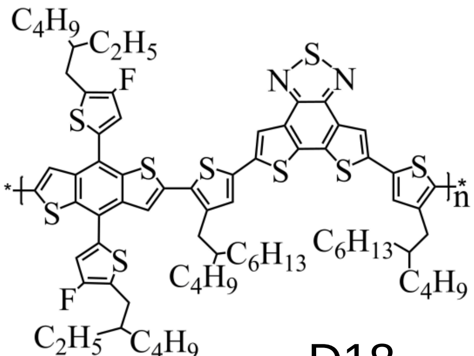
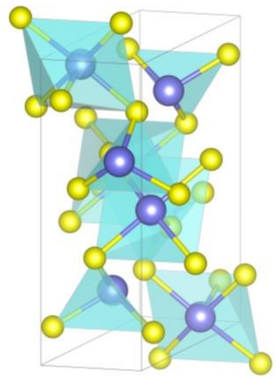
## Organic semiconductors




D18



## Chalcogenides

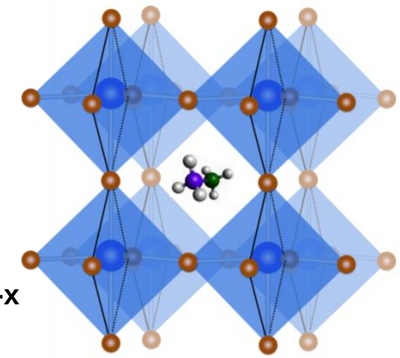
**$Bi_2S_3$**, **$AgBiS_2$**, $NaBiS_2$

$Sb_2S_3$, $AgSbS_2$,

$Sb_2(S,Se)_3$

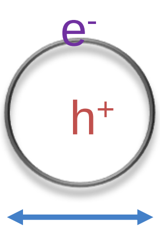
PbS, **$AgInS_2$**, Se, **$Te_xSe_{1-x}$**

## Hybrid perovskites



## Opto-electronic characterization & devices

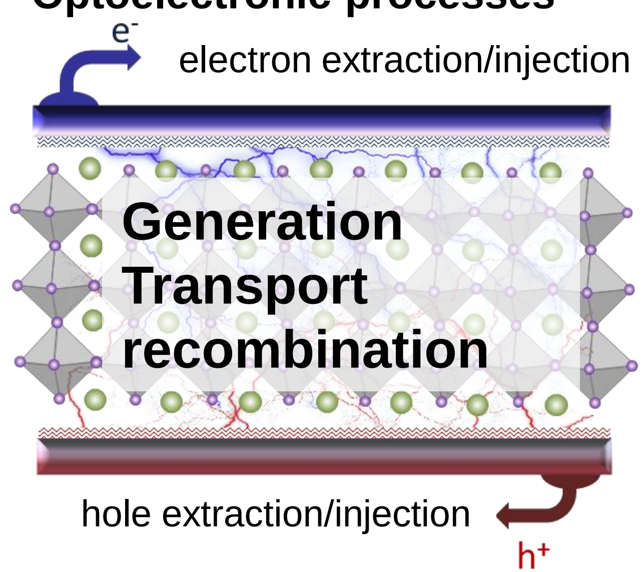
### Optoelectronic properties




$a_{Bohr}$

$n$, $k$, $\sigma$,
$\varepsilon$, $\mu$, $N_A$,
$N_D$, $\tau$, $\gamma$,
$L_D$, $E_b$,
$a_{Bohr}$

### Optoelectronic processes




### Device performance

**Solar cells：**
$V_{oc}$, $J_{sc}$, FF, PCE

**Photodetectors：**
$D$, LDR, $f_{-3dB}$, $J_{noise}$

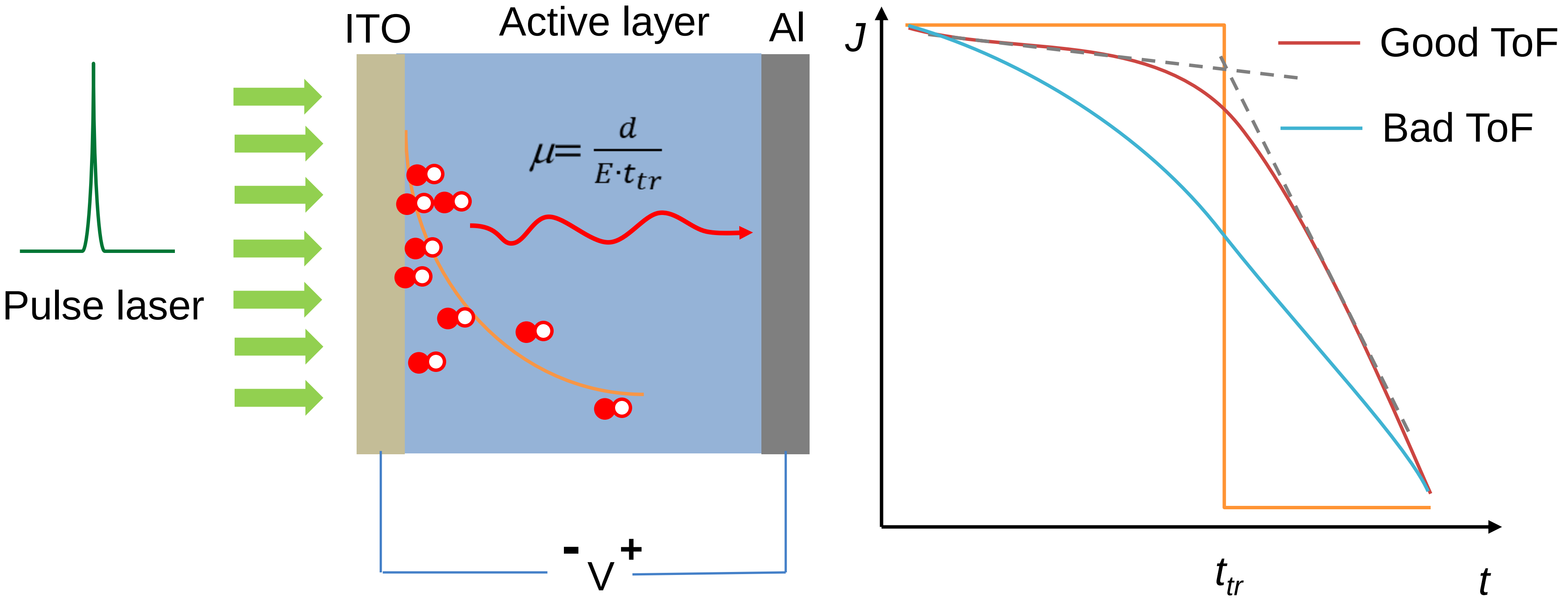
**LEDs：**
Color, $L$, QE, $t_r$,

Y. Xu, **Q. Lin***, *Appl. Phys. Rev.*, **7**: 011315 (2020).

**Q. Lin**, A. Armin, P. Burn*, P. Meredith*, *Acc. Chem. Res.*, **49**: 545-553 (2016).

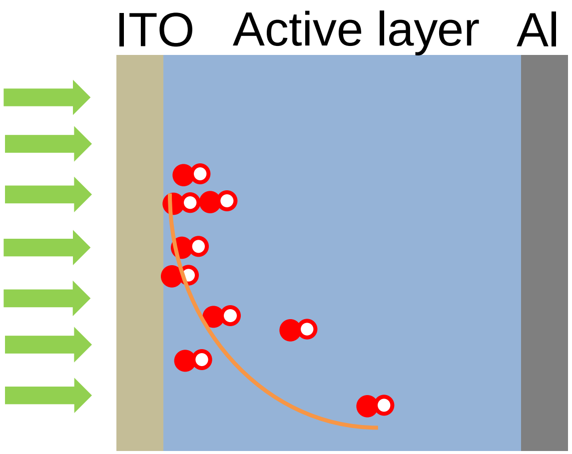
## Time of flight (ToF)

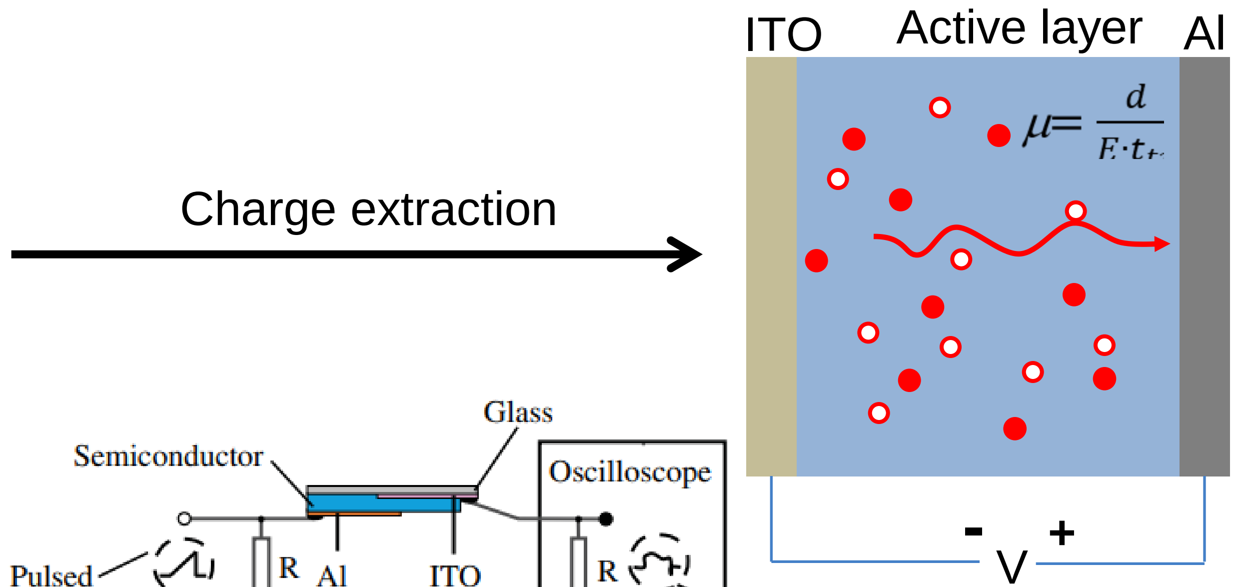
$v = d/t_{tr}$ $\mu = \frac{d}{E \cdot t_{tr}}$

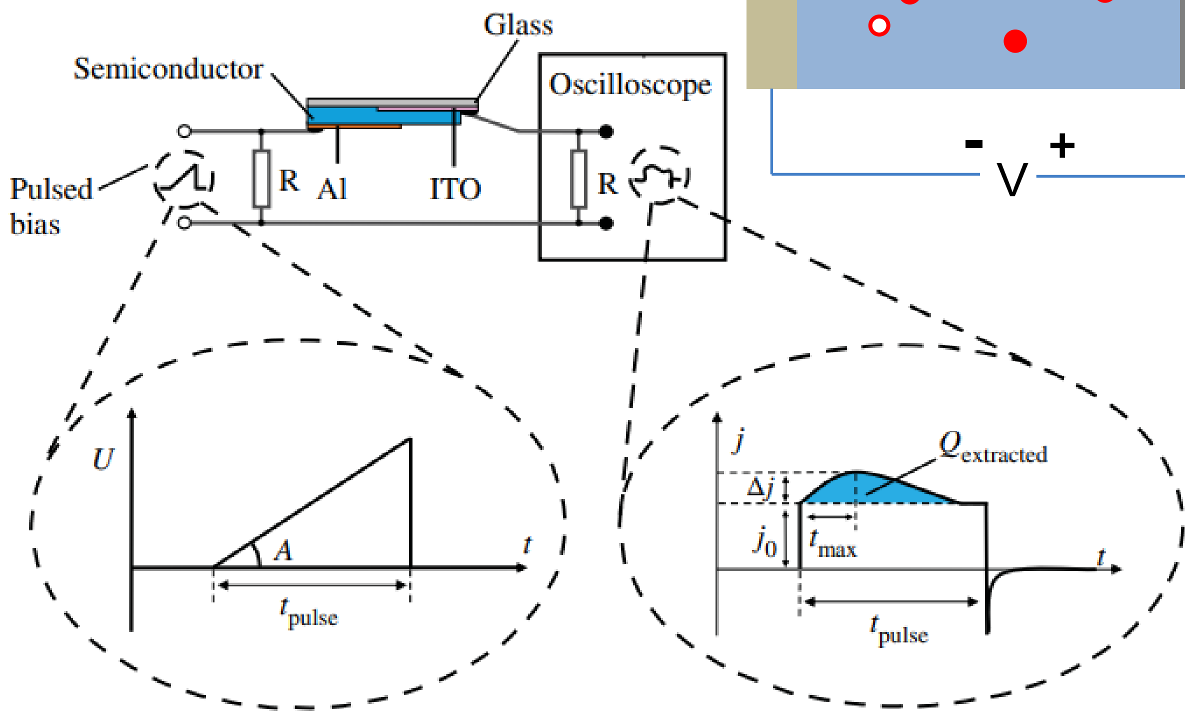



- Carrier generation need to be on the surface with a thick junction
- Mobility is highly dispersive for disordered materials
- Field dependent
- High voltage bias may cause degradation

Charge extraction by linearly increasing voltage (photo-CELIV) $v = d/t_{tr}$ $\mu = \frac{d}{E \cdot t_{tr}}$



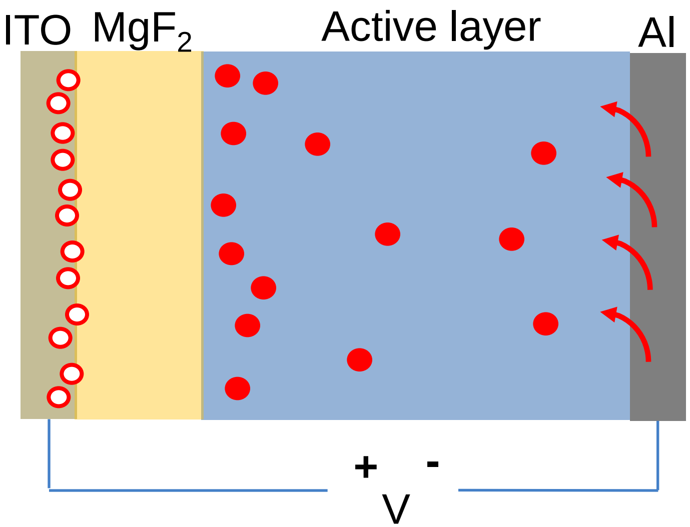



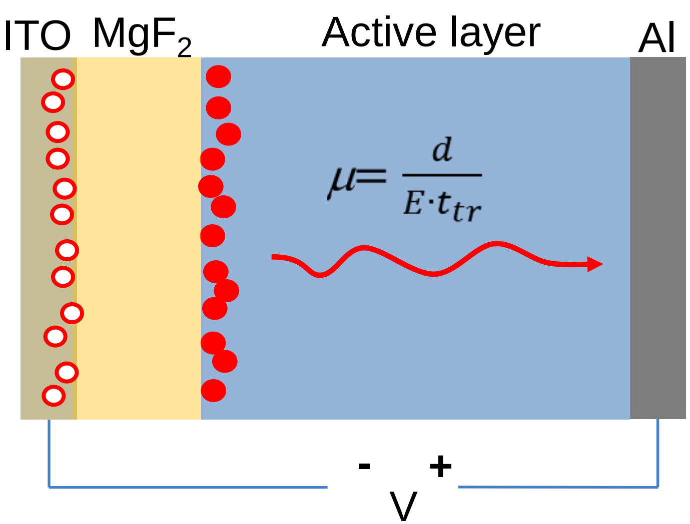



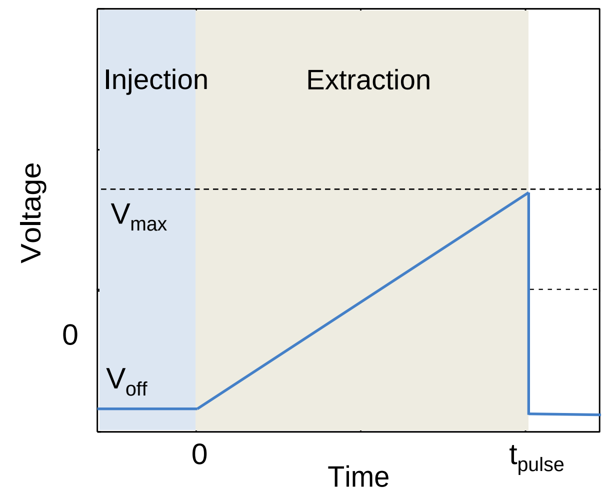

- Mixed mobility
- Photogeneration
- Recombination

Oleksandr Grynko, Gytis Juška, and Alla Reznik, Charge Extraction by Linearly Increasing Voltage (CELIV) Method for Investigation of Charge Carrier Transport and Recombination in Disordered Materials, Photoconductivity and Photoconductive Materials, Volume 1, Wiley (2022).

# Metal-insulator-Semiconductor charge extraction by linearly increasing voltage (MIS-CELIV)

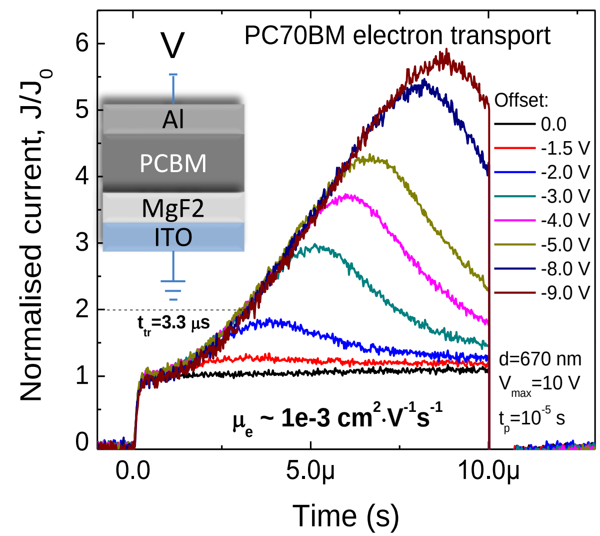



$v = d/t_{tr}$

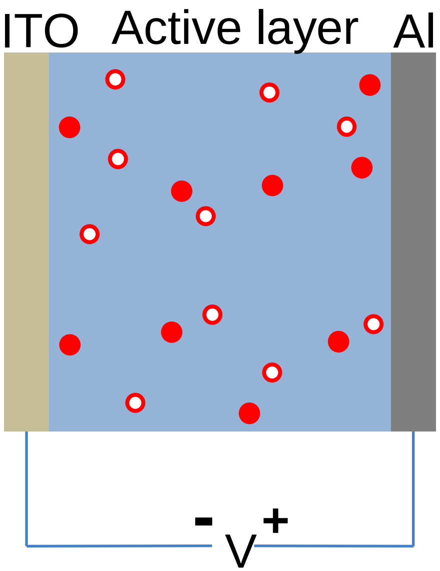
$$\mu = \frac{d}{E \cdot t_{tr}}$$




- ✓ Measure electron and hole mobility separately
- ✓ Reduce dispersive charge transport

Armin A, Juska G, Ullah M, *et al.* Balanced carrier mobilities: not a necessary condition for high-efficiency thin organic solar cells as determined by MIS-CELIV. ***Adv. Energy Mater***., 4: 1300954 (2014).

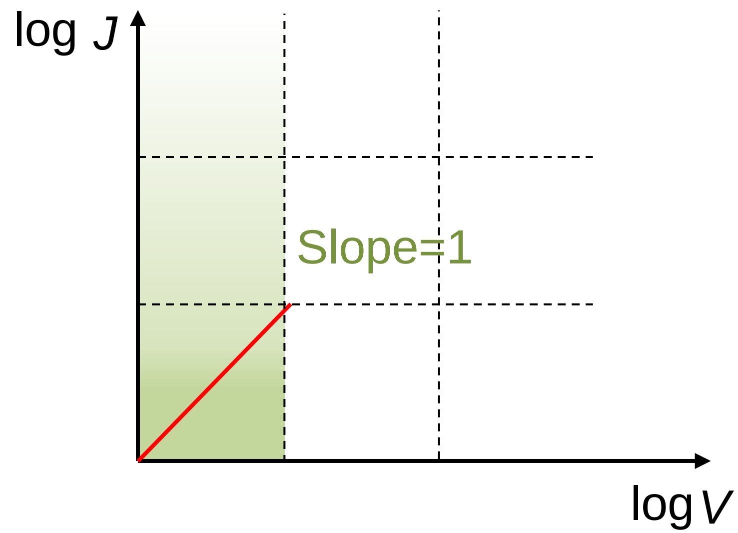
Space charge limited current (SCLC)

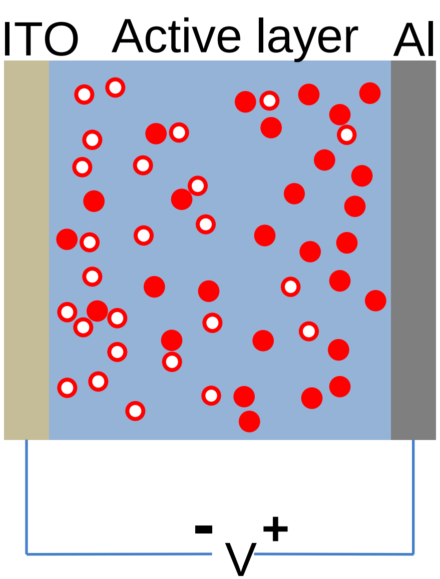



$$\sigma = e \cdot N \cdot \mu$$

$$E = \frac{V}{d}$$

$$J = E \cdot \sigma = \frac{V \cdot e \cdot N \cdot \mu}{d}$$



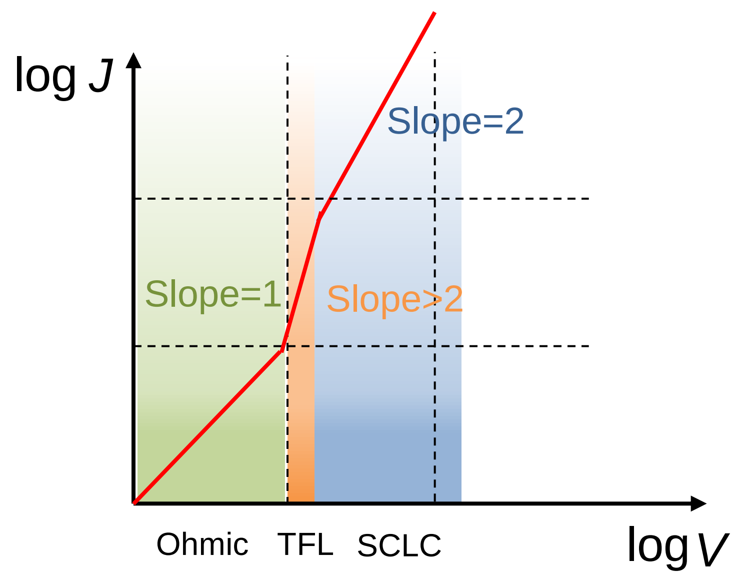




$$Q = C \cdot V$$

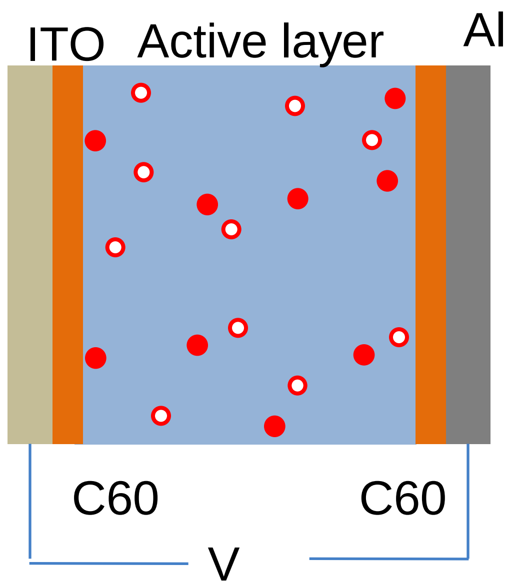
$$\mu = \frac{d}{E \cdot t_{tr}}$$

$$J = \frac{Q}{t_{tr}} = \frac{C \cdot V}{t_{tr}}$$

$$J \propto \frac{\varepsilon \cdot \mu \cdot V^2}{d^3}$$

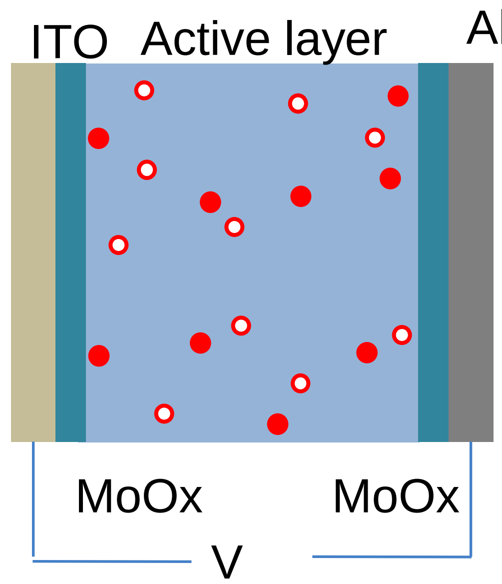


Electron only device

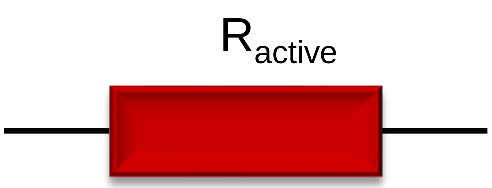



- Ohmic contact
- Trap states
- Conductivity
- Series resistance

Hole only device

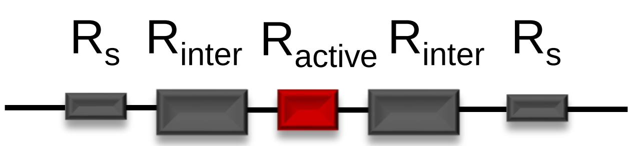



Ideal SCLC



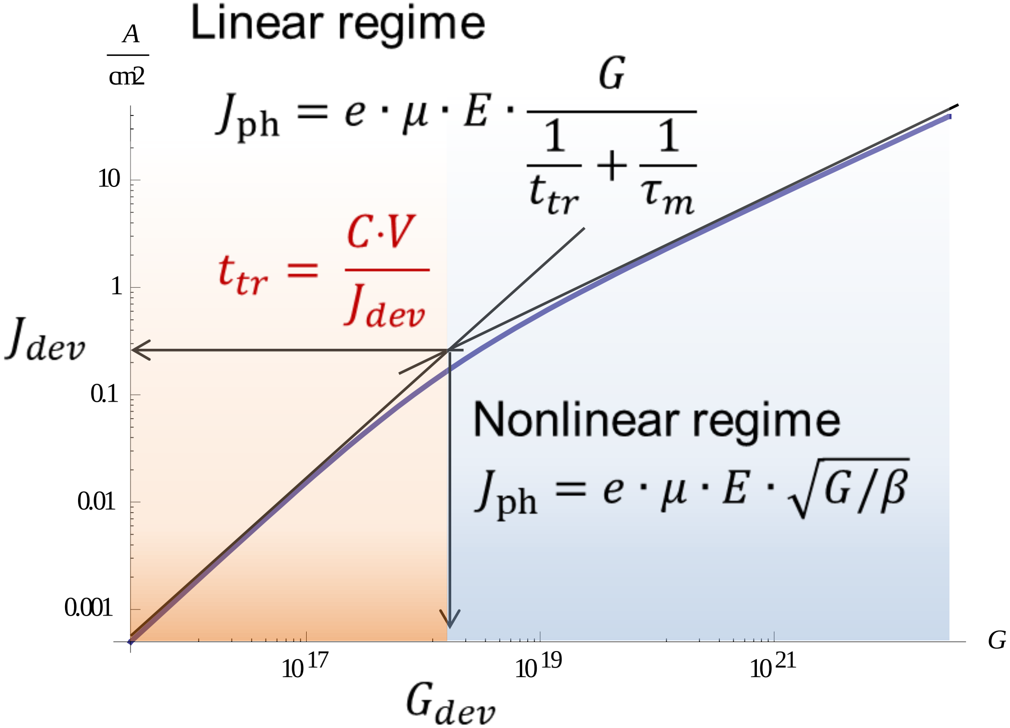

Real SCLC

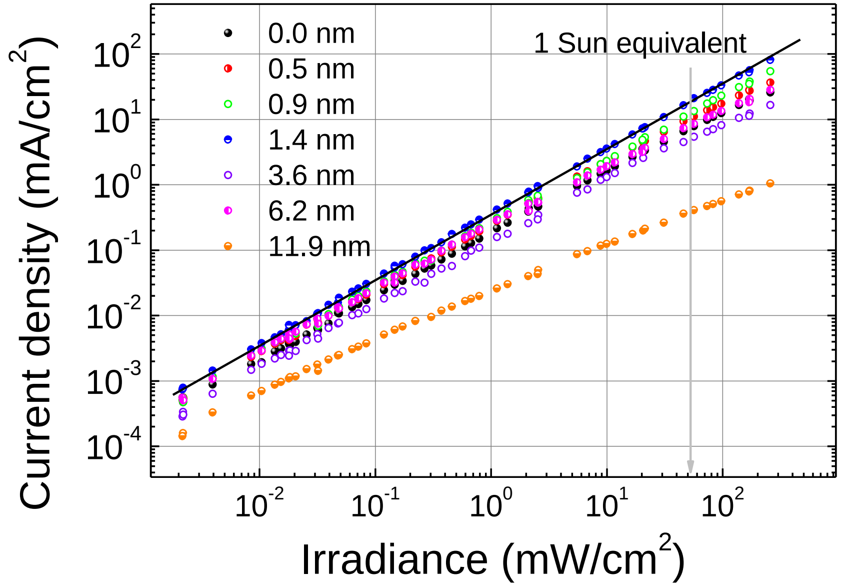

Non-ideal SCLC

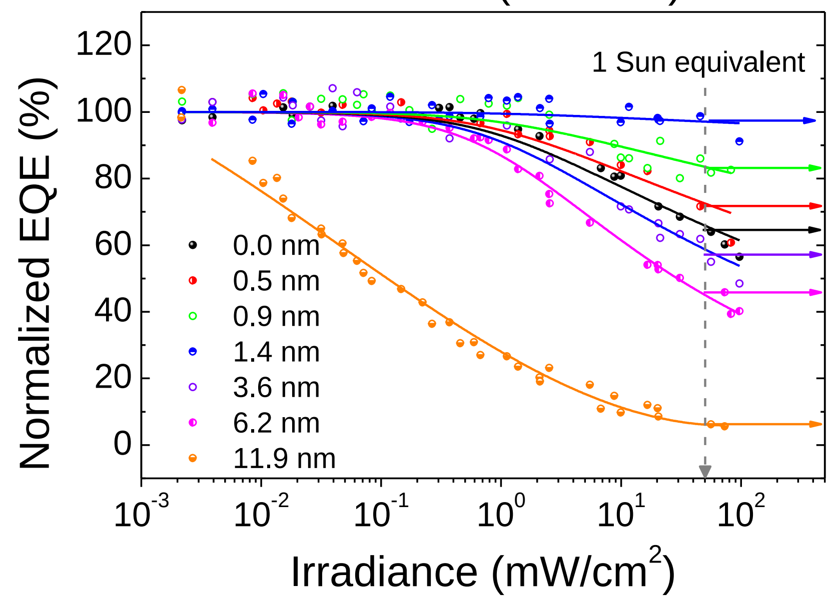


# Light intensity dependent photocurrent

## Deviation from linearity




This is important in Linear Dynamic Range of photodetectors and also Power Conversion Efficiency of solar cells.

**Qianqian Lin**, Dani M. Stoltzfus, Ardalan Armin, Paul L. Burn*, Paul Meredith*. An hydrophilic anode interlayer for solution processed organohalide perovskite solar cells. ***Advanced Materials Interfaces***, 3: 1500420 (2016).

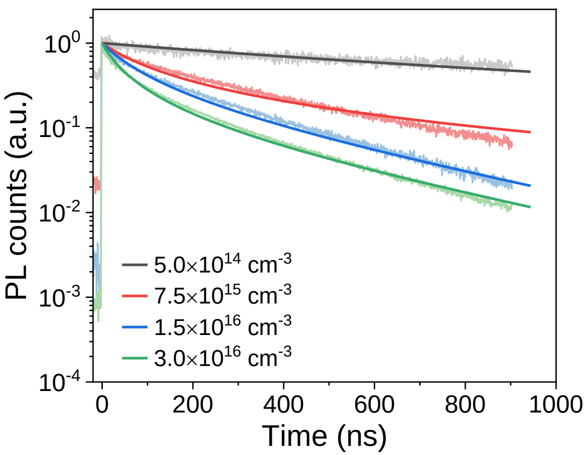
- Time-resolved Photoluminescence:

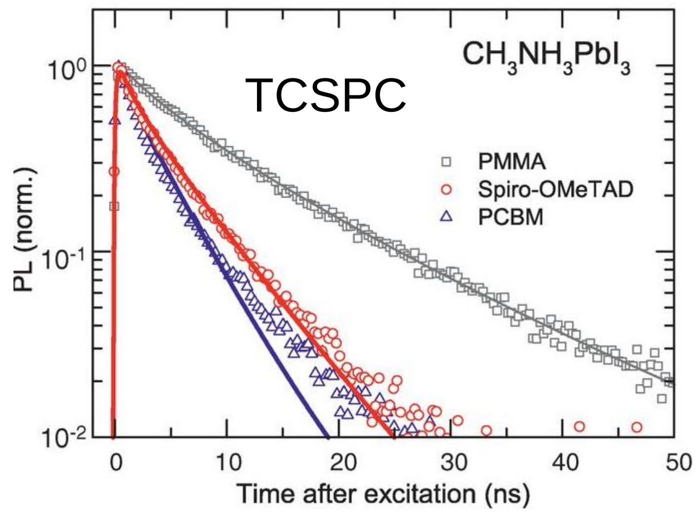
**Time-correlated single photon counting (TCSPC):** high time resolution, poor spectra;

**Gated intensified CCD (iCCD) spectroscopy**: excellent spectra, poor time resolution;

**Streak camera**: excellent spectra, fast response, high price;

**Femtosecond photoluminescence upconversion (fs PLUC)**: sub-picosecond resolution (100 fs), very low detectivity.




$$D = \mu \frac{kT}{e}$$

$$L = \sqrt{D\tau}$$

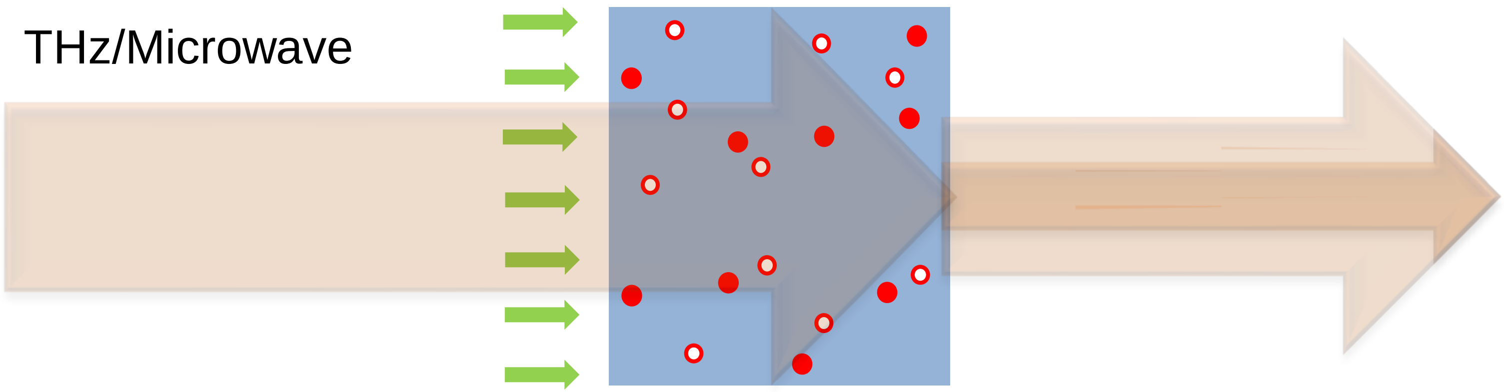
$$\frac{dn}{dt} = G - k_1 n - k_2 n^2 - k_3 n^3$$

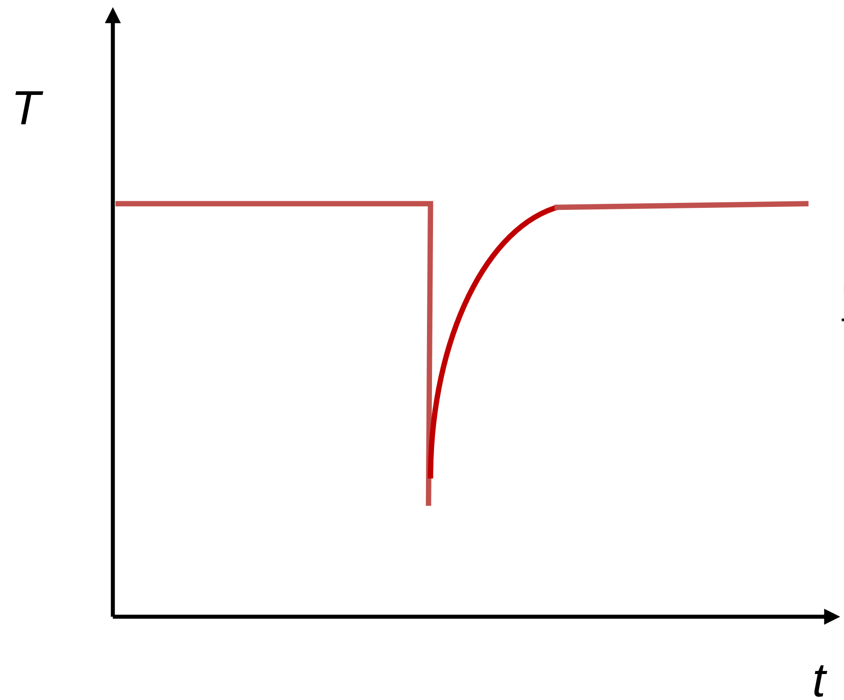
$$\frac{\partial n(x,t)}{\partial t} = D\frac{\partial^2 n(x,t)}{\partial x^2} - k(t)n(x,t)$$

Lifetime, recombination rates, diffusion length

Stranks S D *et al*. **Science**, 342(6156): 341-344 (2013).

- Time-resolved microwave conductivity (TRMC):



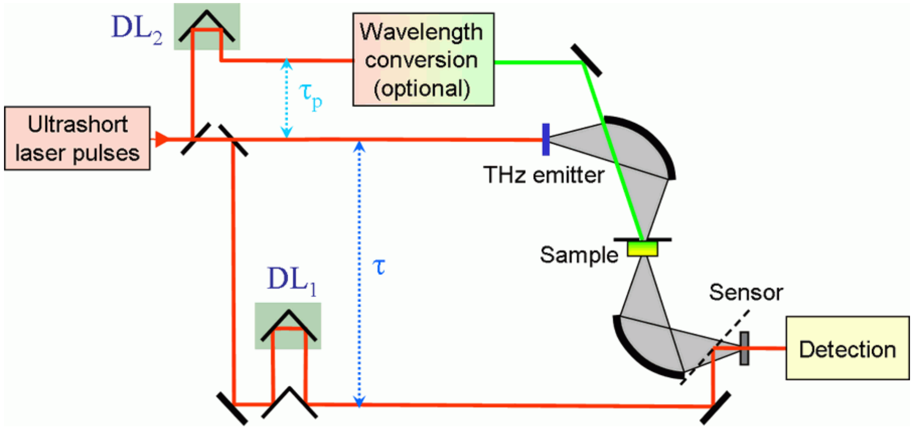



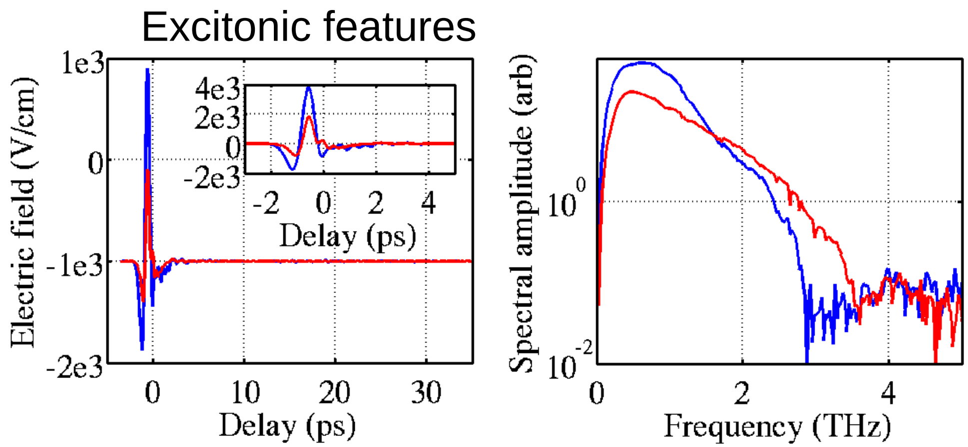

Lifetime:

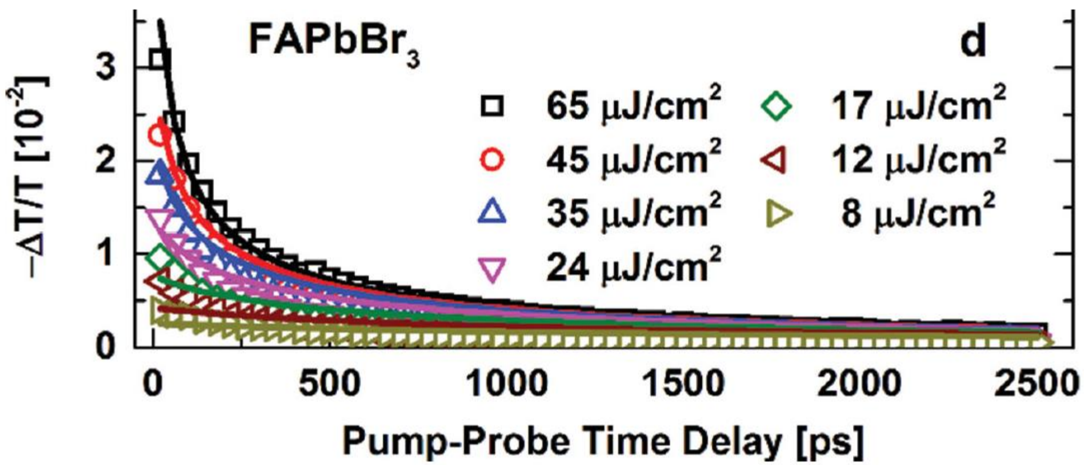
$$\frac{dn}{dt} = G - E - R = -R_{\mathrm{rad}} - R_{non\text{-}\mathrm{rad}}$$

Sensitive to all carriers

- Optical pump THz-probe spectroscopy:



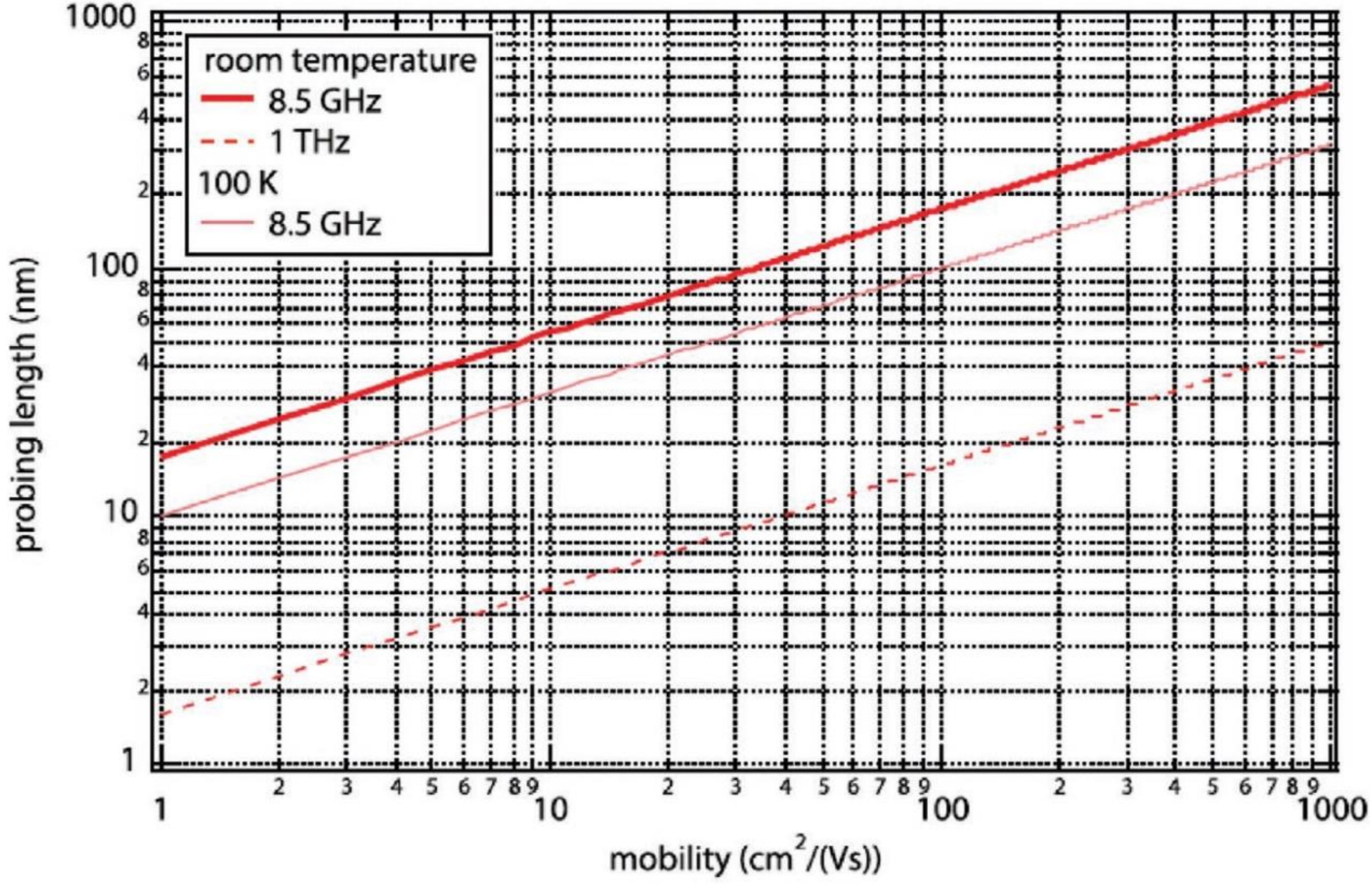

$$\frac{dn}{dt} = -k_3 n^3 - k_2 n^2 - k_1 n$$

$$\Delta S = -\varepsilon_0 c\,(n_a + n_b)\frac{\Delta T}{T}$$

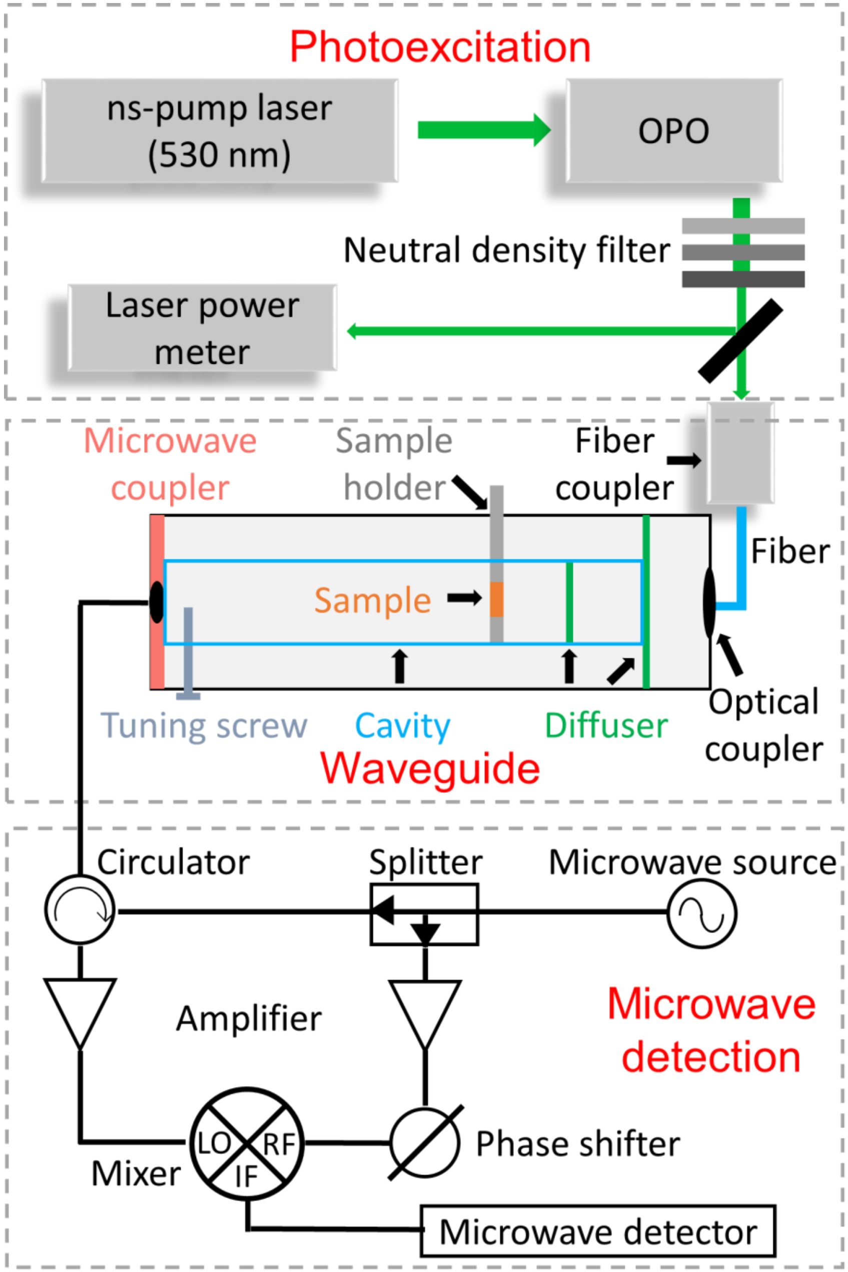
$$\mu = \frac{\Delta S\, A_{eff}}{N\, e} \qquad D = \frac{\mu k_B T}{e} \qquad L_D(n) = \sqrt{\frac{D}{R_{total}(n)}}$$

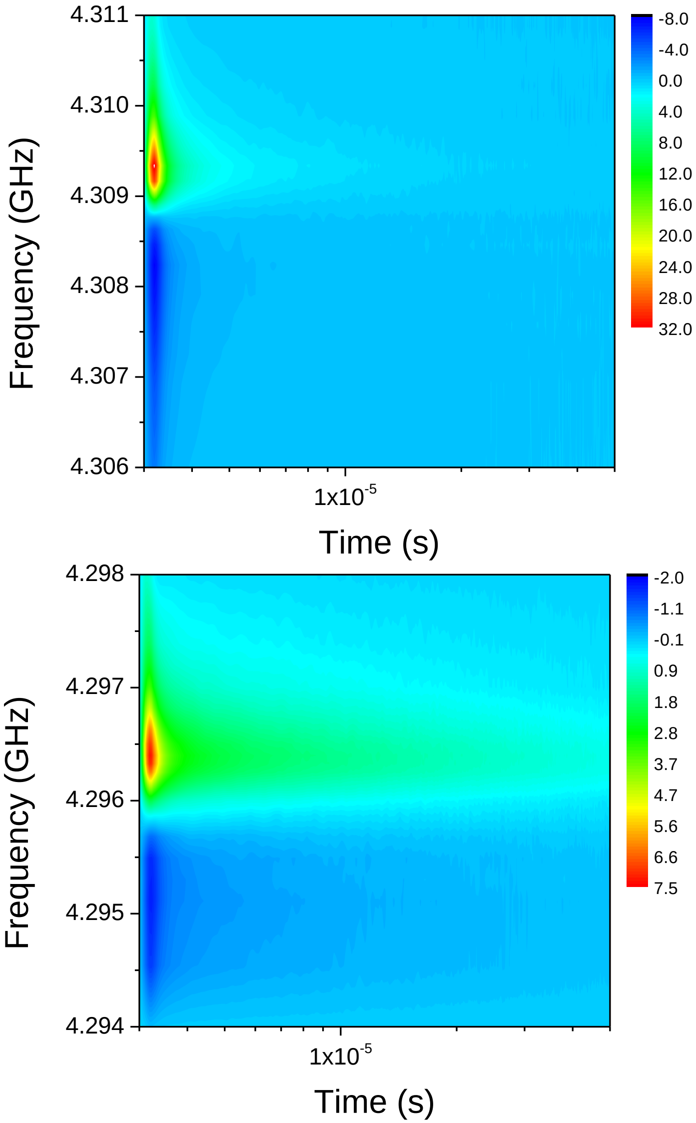
Lin Q. *et al*. **Adv. Funct. Mater.** 2017, 27(38): 1702485.
Rehman W. *et al*. **Adv. Mater**. 2015, 27(48): 7938-7944.

TRMC & OPTP



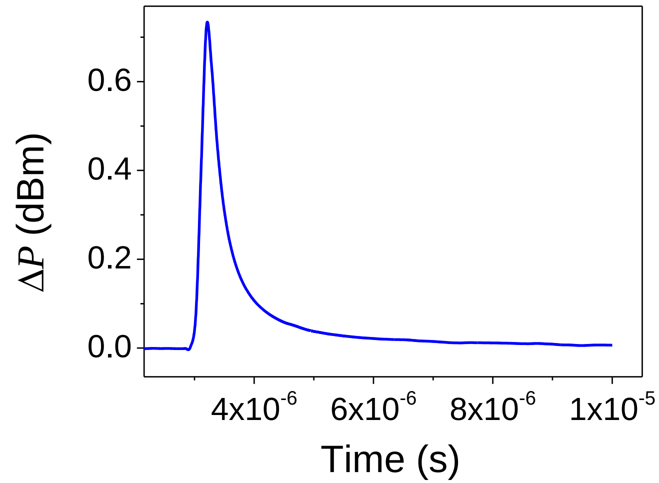

T. Savenije *et al.*, **Adv. Mater.** 2020, 1903788.



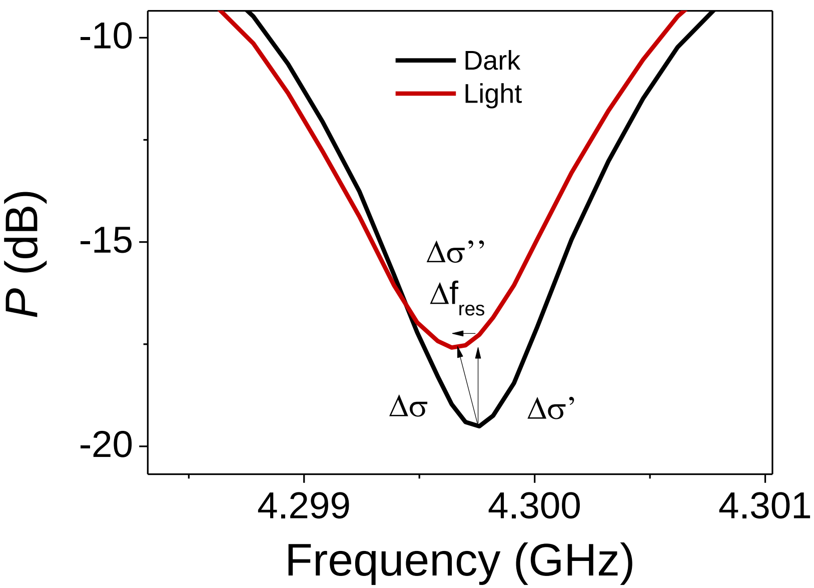



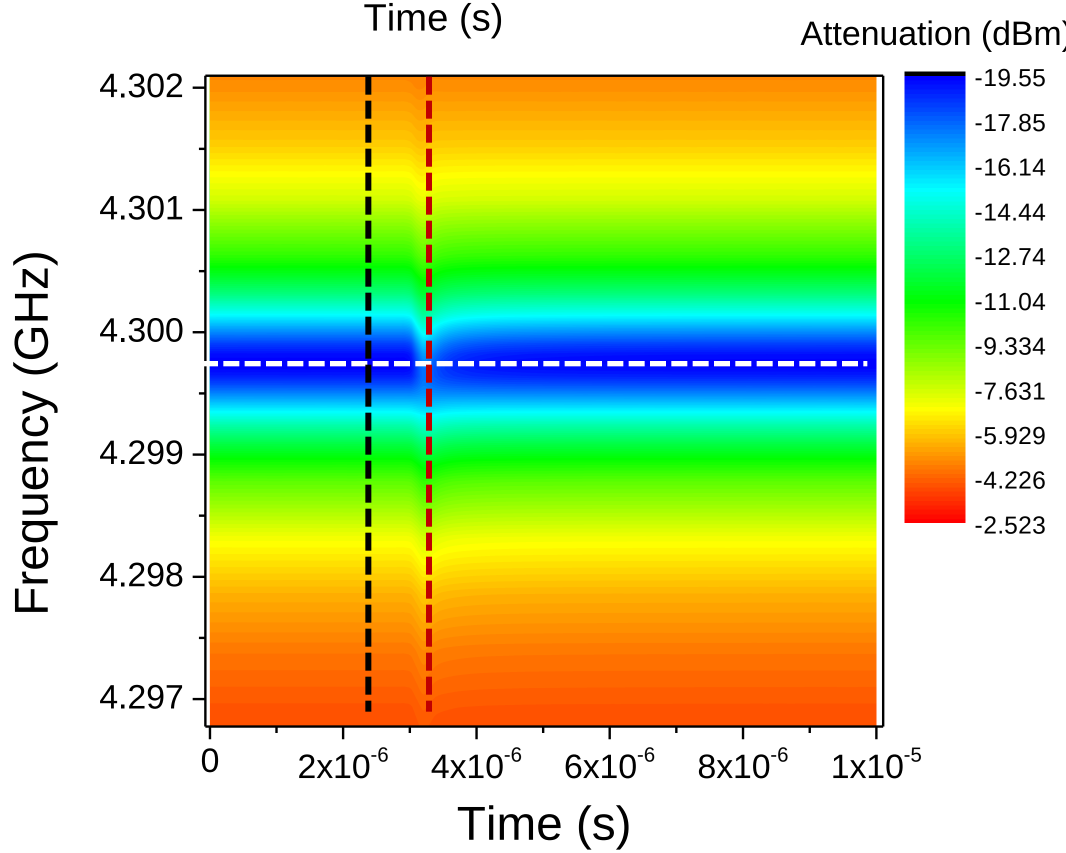

R.Li, Q. Lin* *et al*., ***J. Phys. Chem. Lett.***, 12: 1726-1733 (2021).
F. Yao*, Q. Lin*, ***ACS Photonics***, 12:2103652 (2022).
Y. Li, Q. Lin*, ***Appl. Phys. Rev.***, 10:011406 (2023).

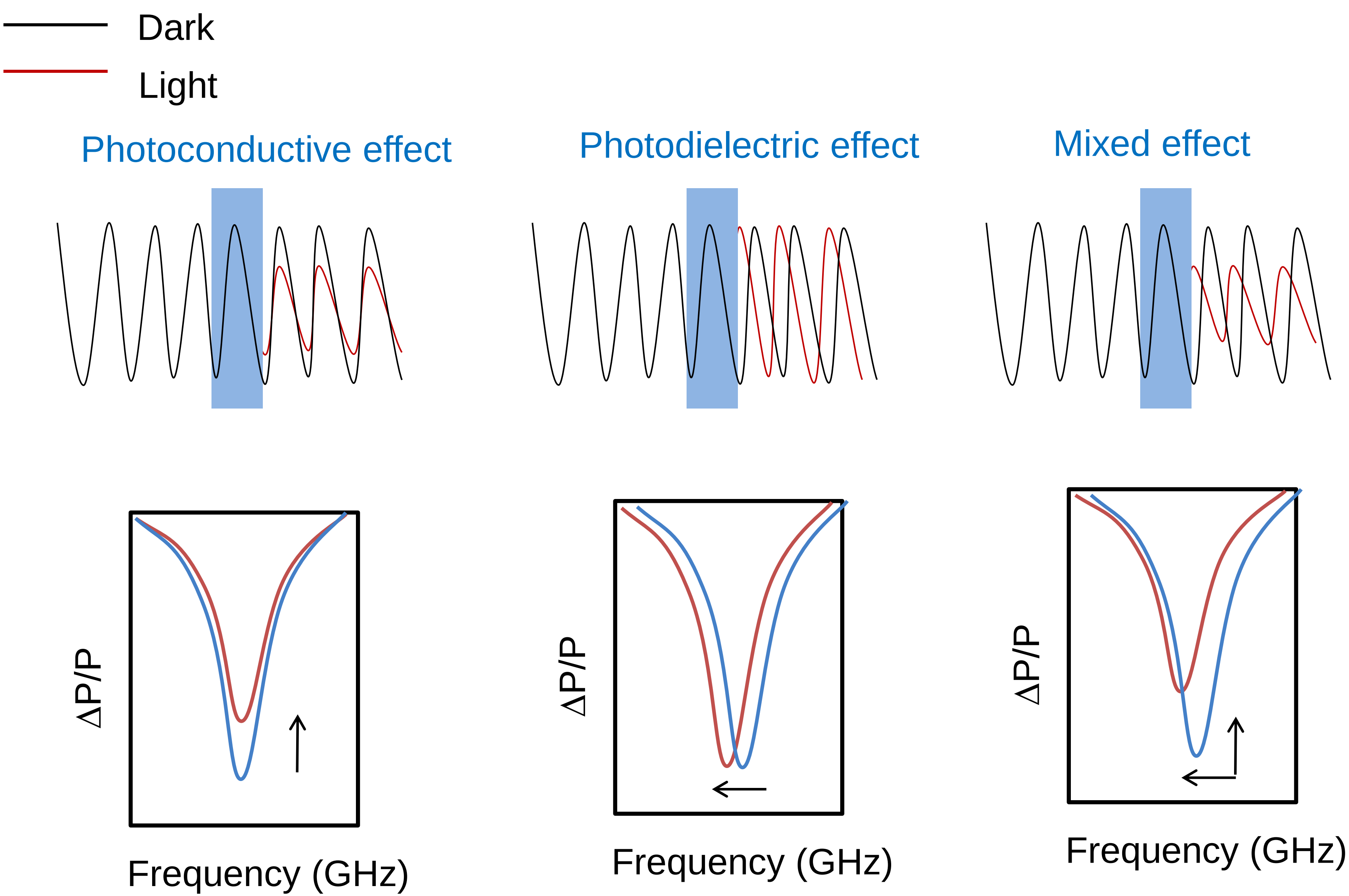
1. TRMC dynamics

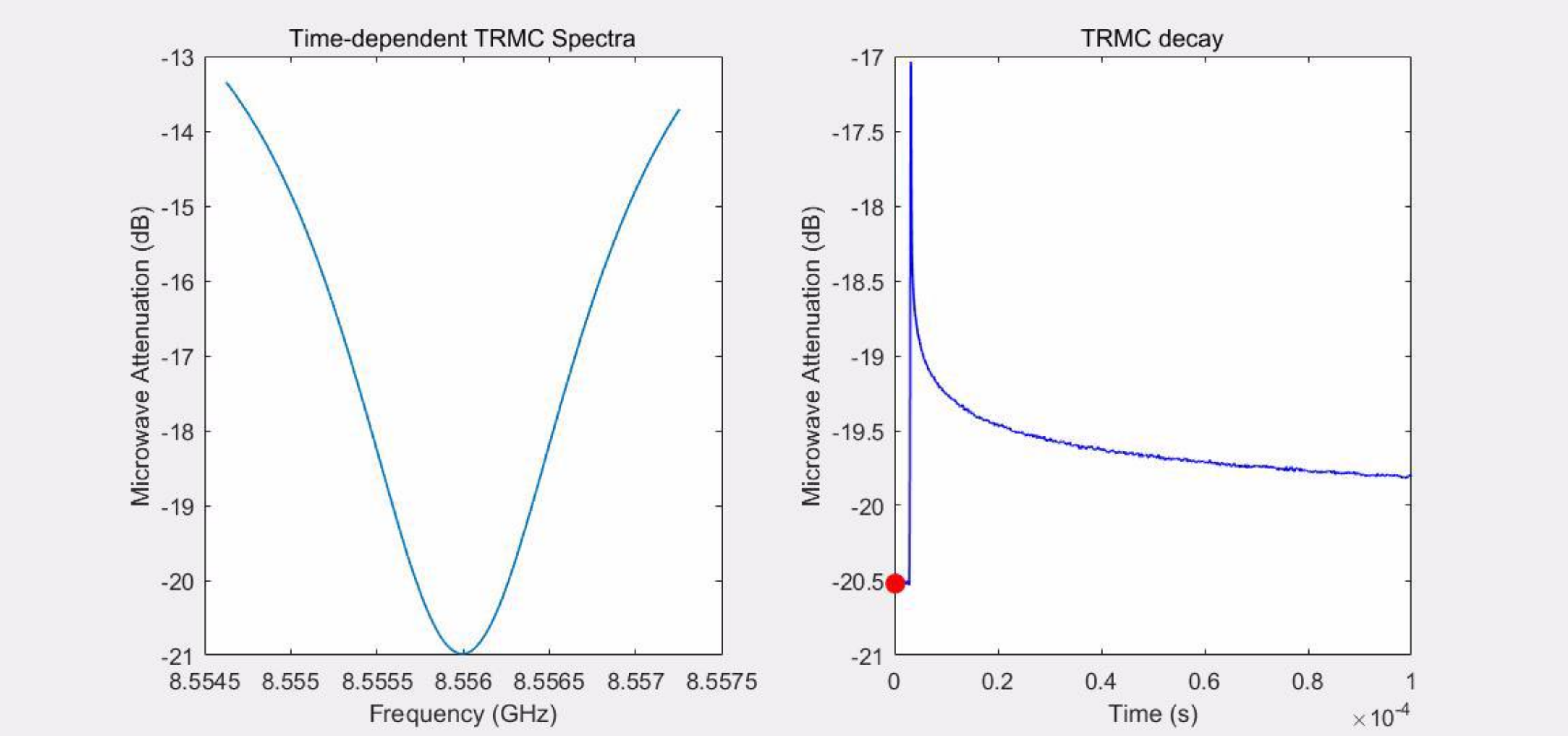



2. TRMC Spectra：
(complex conductivity,
phase information)

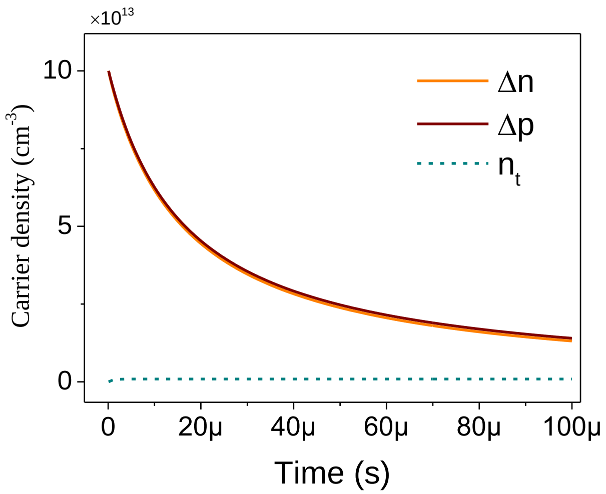


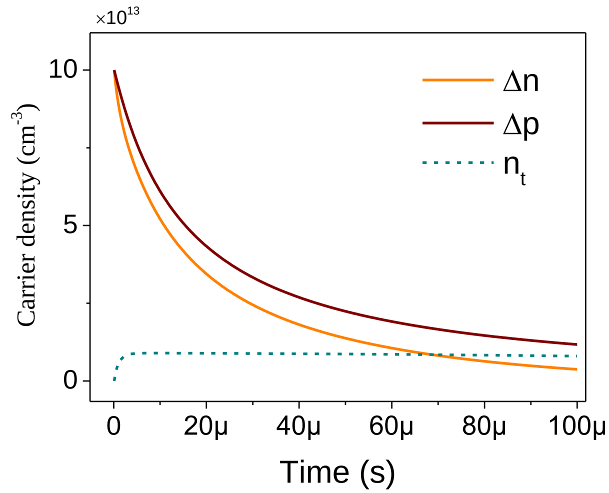

Dark
Light
Photoconductive effect
Photodielectric effect
Mixed effect
ΔP/P
Frequency (GHz)
ΔP/P
Frequency (GHz)
ΔP/P
Frequency (GHz)


Time-dependent TRMC Spectra
Microwave Attenuation (dB)
-13
-14
-15
-16
-17
-18
-19
-20
-21
8.5545
8.555
8.5555
8.556
8.5565
8.557
8.5575
Frequency (GHz)
TRMC decay
Microwave Attenuation (dB)
-17
-17.5
-18
-18.5
-19
-19.5
-20
-20.5
-21
0
0.2
0.4
0.6
0.8
1
Time (s)
× 10^-4

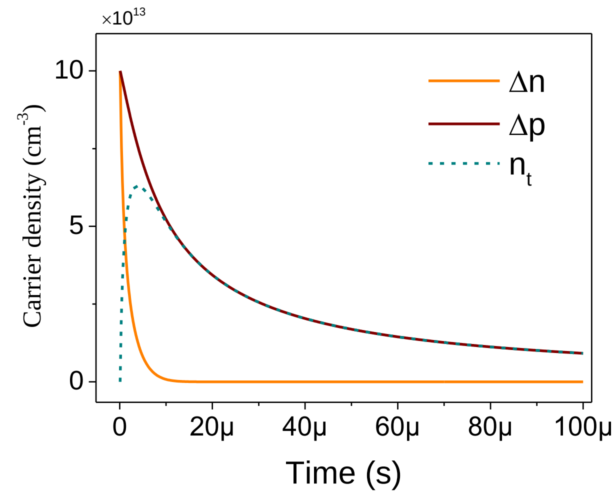
Nt=1e12 cm$^{-3}$




Nt=1e13 cm$^{-3}$




Nt=1e14 cm$^{-3}$



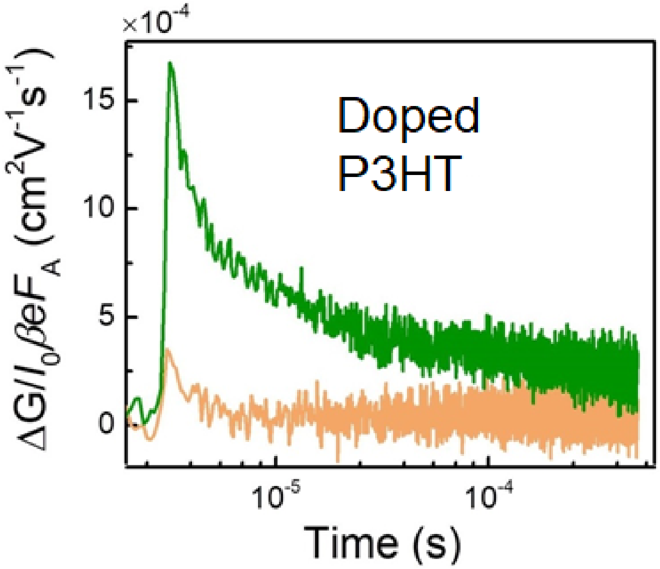

# Continuous equation

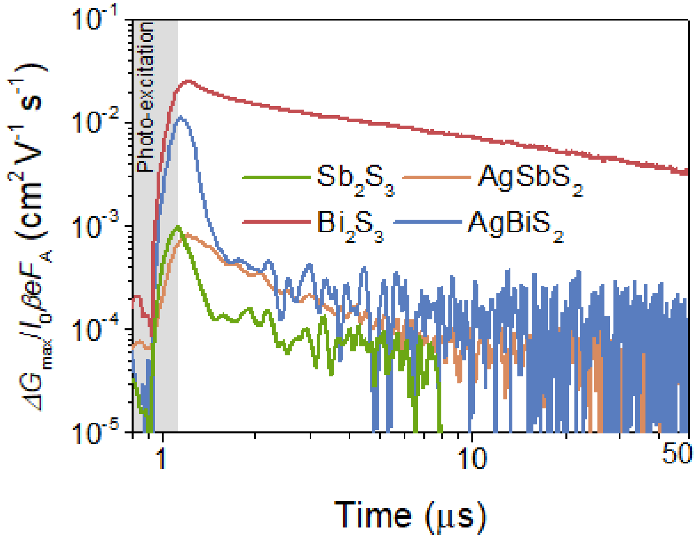
Density of trap state

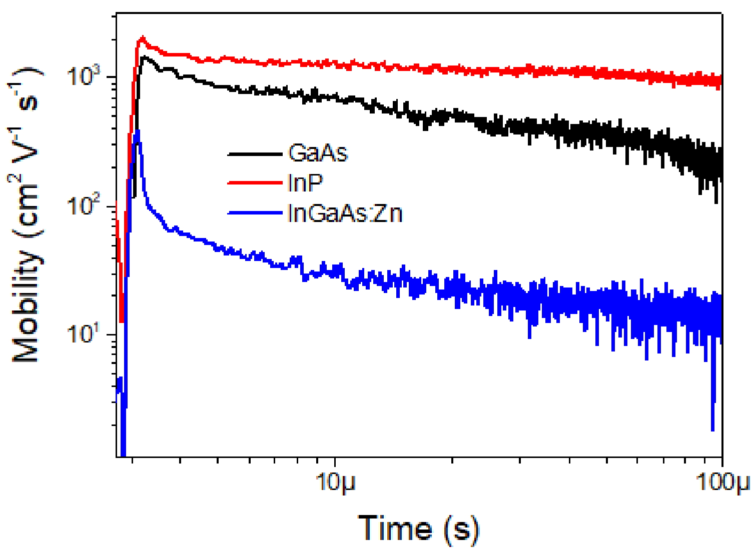
$$\frac{d\Delta n}{dt} = G_c - k_2 \Delta n(\Delta p + p_0) - k_T \Delta n(N_T - n_t)$$

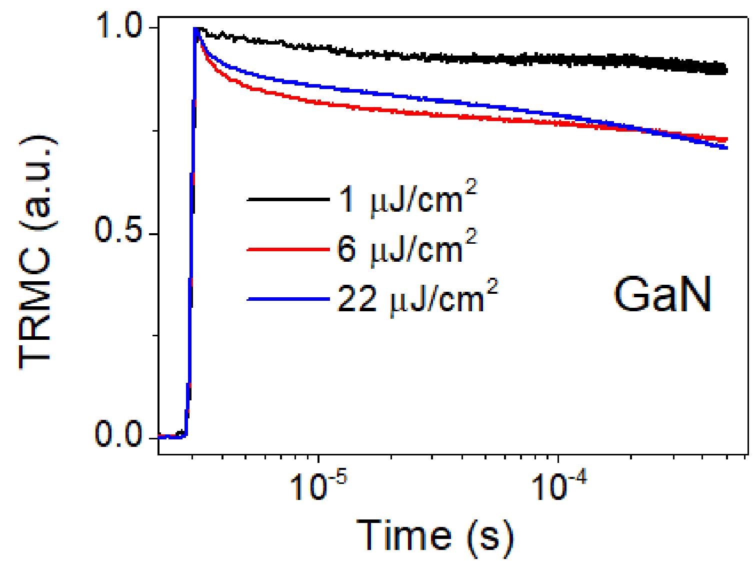
$$\frac{d\Delta p}{dt} = G_c - k_2 \Delta n(\Delta p + p_0) - k_D n_t(\Delta p + p_0)$$

$$\frac{dn_t}{dt} = k_T \Delta n(N_T - n_t) - k_D n_t(\Delta p + p_0)$$



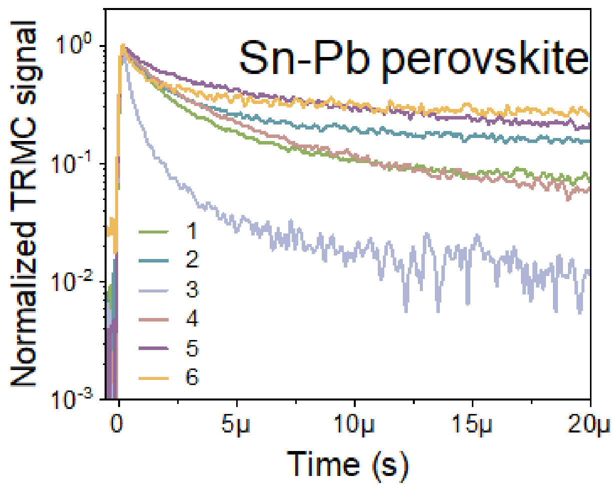



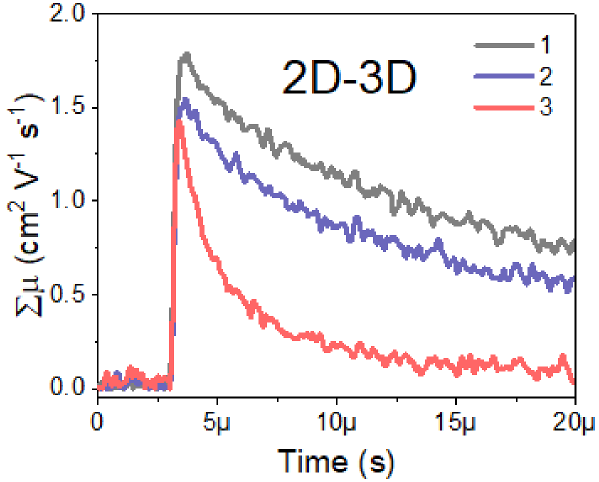

Q. Lin* *et al.*, ***Nat. Commun.***, **2021**, 12: 1531.

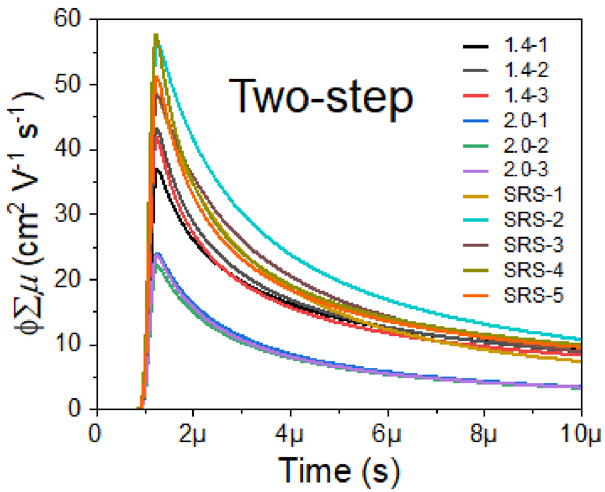
Q. Lin* *et al.*, ***Appl. Phys. Rev.***, **2022**, 9: 021405.

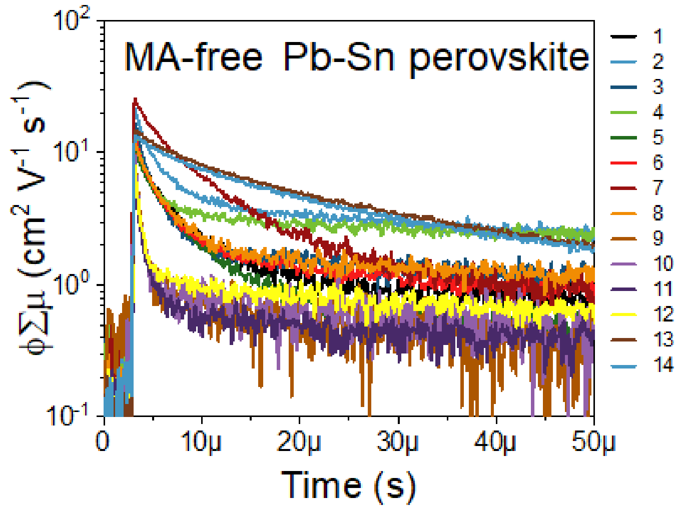
Q. Lin* *et al.*, **ACS Energy Lett.**, 2023, 8: 1485-1492.

Q. Lin* *et al.*, ***Matter***, **2022**, 5: 2251-2264.

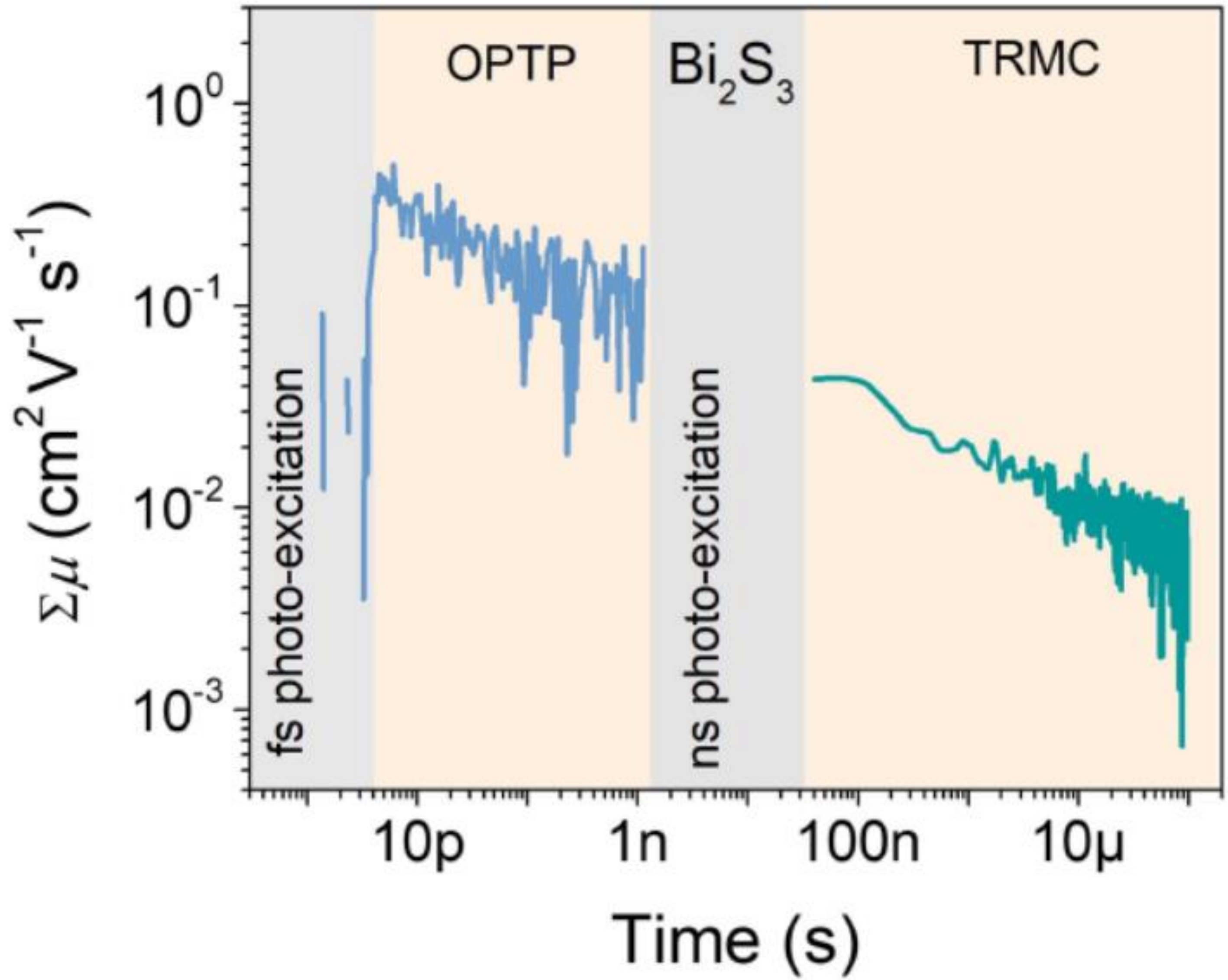



***Nature Energy, 2023,*** DOI:10.1038/s41560-023-01274-z.
***Nature Energy, 2023,*** DOI:10.1038/s4156-023-01295-8.
***Nature Energy***, ***2023,*** DOI:10.1038/s41560-023-01377-7.
***Advanced Materials***, ***2023***, 35:2300352.
***Angewandte Chemie***, ***2023***, 62:e202300759.
***Energy & Environmental Science***, ***2023***, DOI: 10.1039/D3EE00869J.

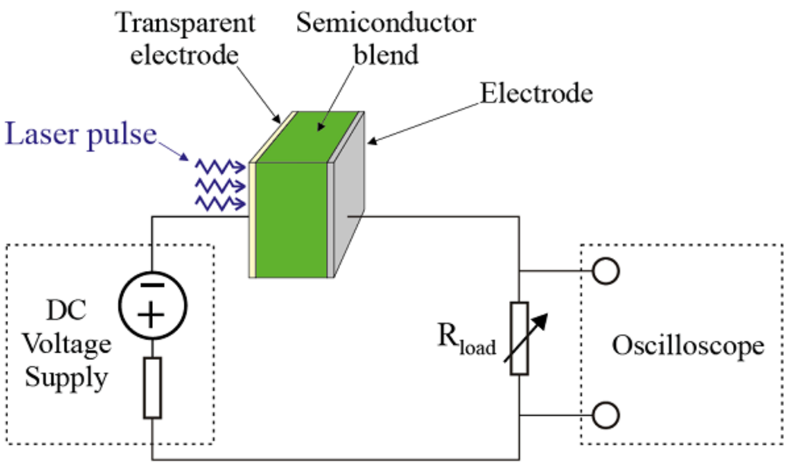



Q. Lin* *et al*., **ACS Energy Lett.,** 2023, 8: 1485-1492.

## Electrical probe

Lon- range charge transport could be slowed down by the grain boundaries and also electrode interfaces
Oscilloscopes can even not record the transients, if they are too fast (RC limited).

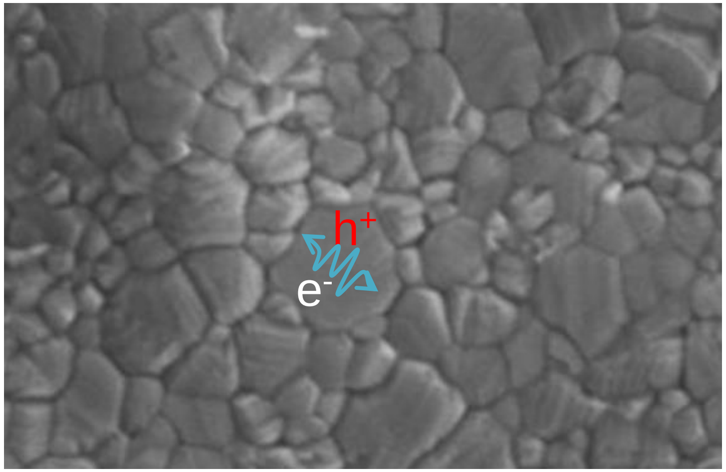
Used to underestimate the mobility



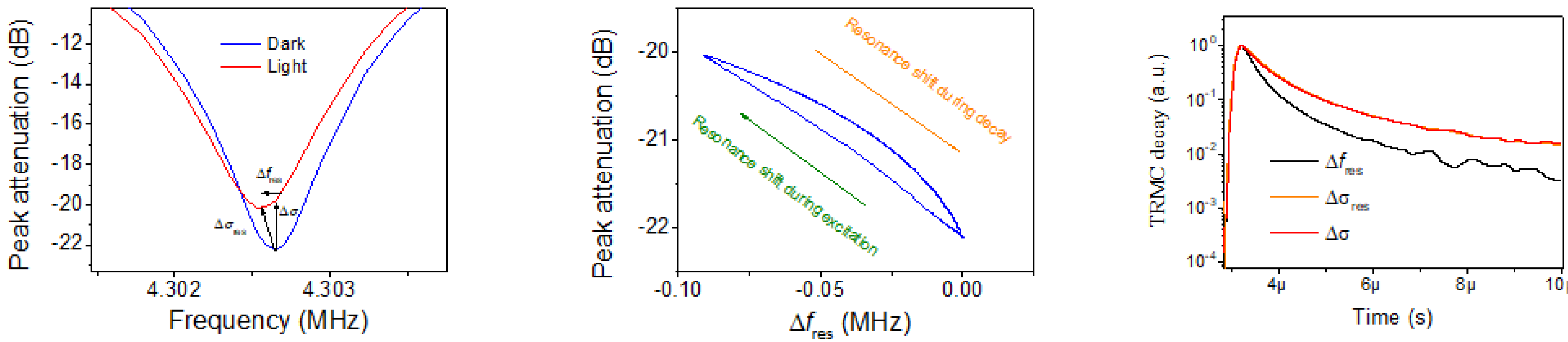

## Optical probe

Short range within the crystals without the effect of grain boundaries

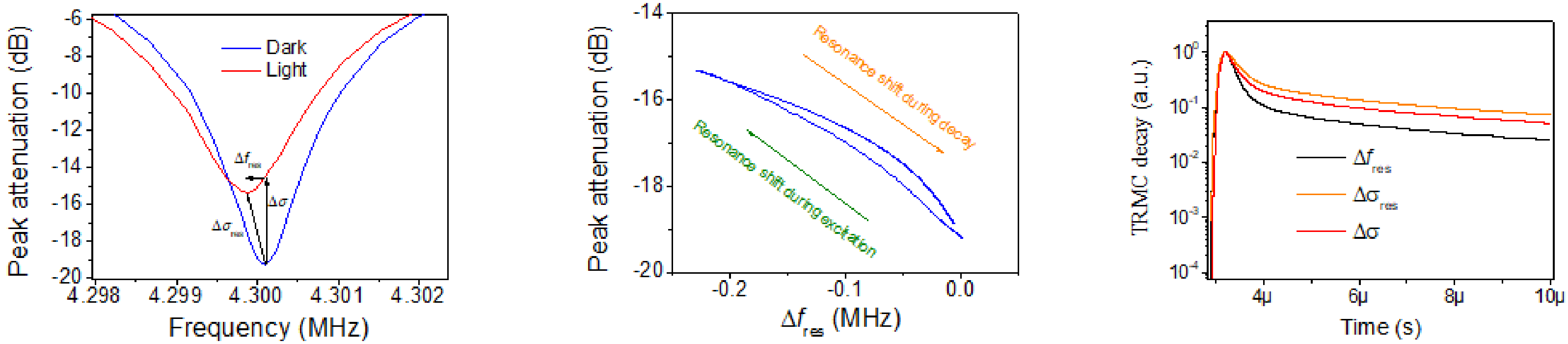
Used to overestimate the mobility



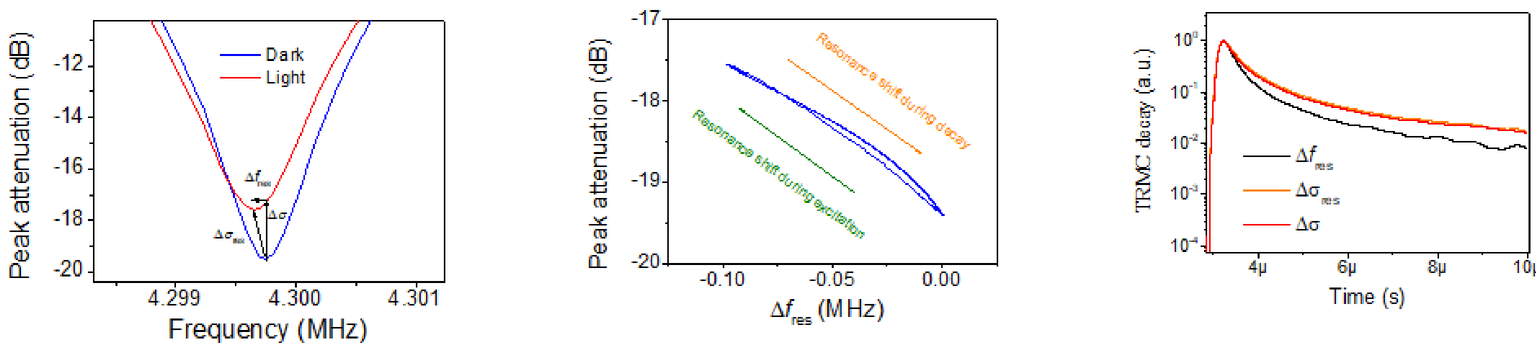
## Perovskite 1




## Perovskite 2




## Perovskite 3



## Drude-Smith Model

$$\Delta\sigma_{DS}'(\omega) = \varepsilon_0 {\omega_p}^2 \frac{\tau}{1+(\omega\tau)^2}\left[1 + c\frac{1-(\omega\tau)^2}{1+(\omega\tau)^2}\right]$$

$$\Delta\sigma_{DS}''(\omega) = \varepsilon_0 {\omega_p}^2 \frac{\omega\tau^2}{1+(\omega\tau)^2}\left[1 + \frac{2c}{1+(\omega\tau)^2}\right]$$

## Drude-Zener Model

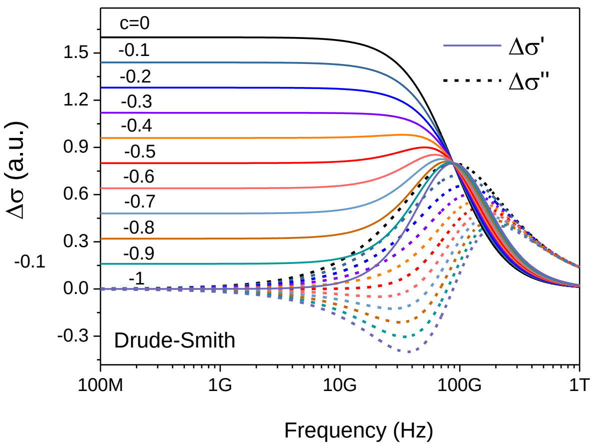
$$\Delta\sigma_{DZ,trap}'(\omega) = \frac{\varepsilon_0 {\omega_p}^2 \omega^2}{\tau} \frac{1}{({\omega_0}^2-\omega^2)^2 + \left(\frac{\omega}{\tau}\right)^2}$$

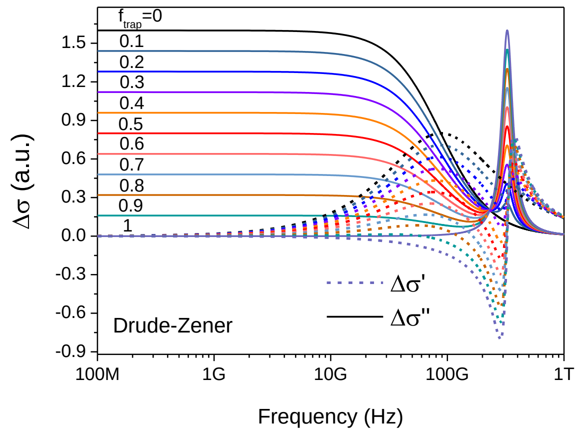
$$\Delta\sigma_{DZ,trap}''(\omega) = -\varepsilon_0 {\omega_p}^2 \omega \frac{{\omega_0}^2-\omega^2}{({\omega_0}^2-\omega^2)^2 + \left(\frac{\omega}{\tau}\right)^2}$$

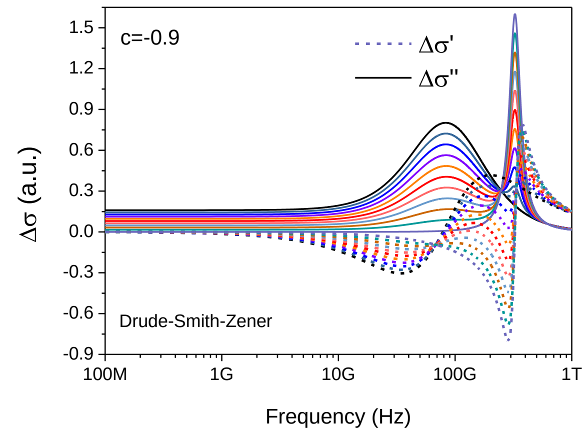
## Mixed Model by Seki *et al.*

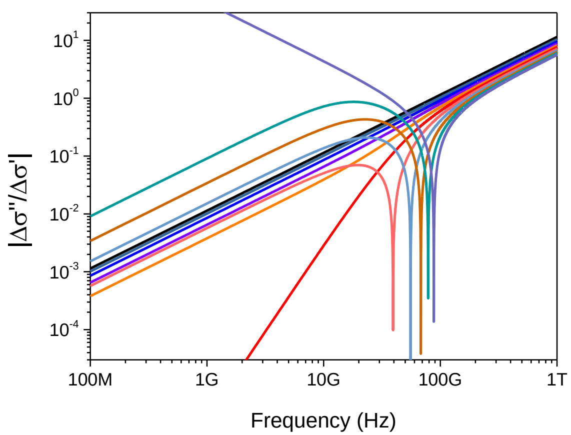
$$\Delta\sigma'(\omega) = (1-f_{trap})\Delta\sigma_{DS}'(\omega) + f_{trap}\Delta\sigma_{DZ,trap}'(\omega)$$

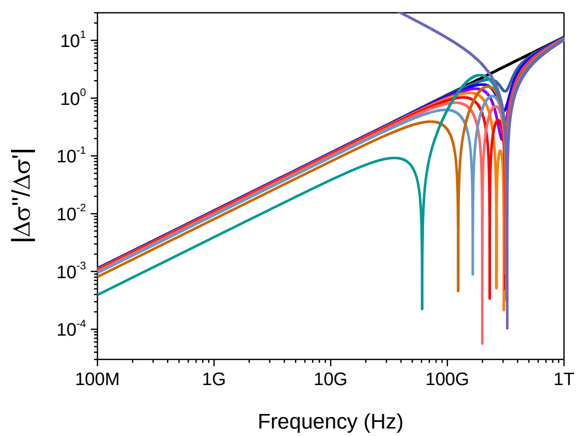
$$\Delta\sigma''(\omega) = (1-f_{trap})\Delta\sigma_{DS}''(\omega) + f_{trap}\Delta\sigma_{DZ,trap}''(\omega)$$

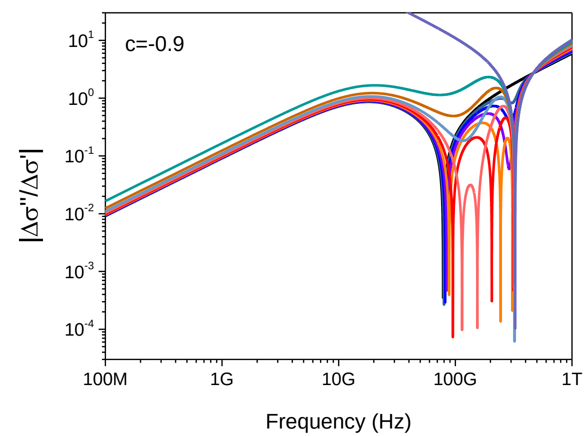


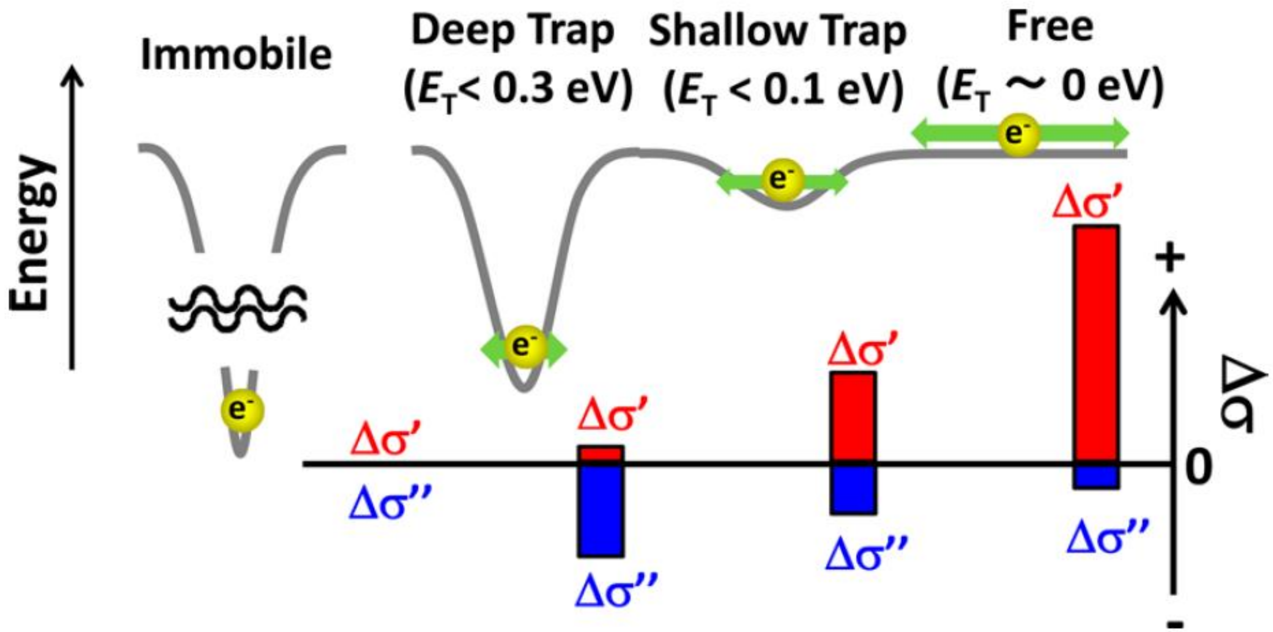






$$\omega_0^{\ 2} = \frac{2}{m^*}\frac{(4\pi\varepsilon_0)^2}{e^4}E_T^{\ 3}$$

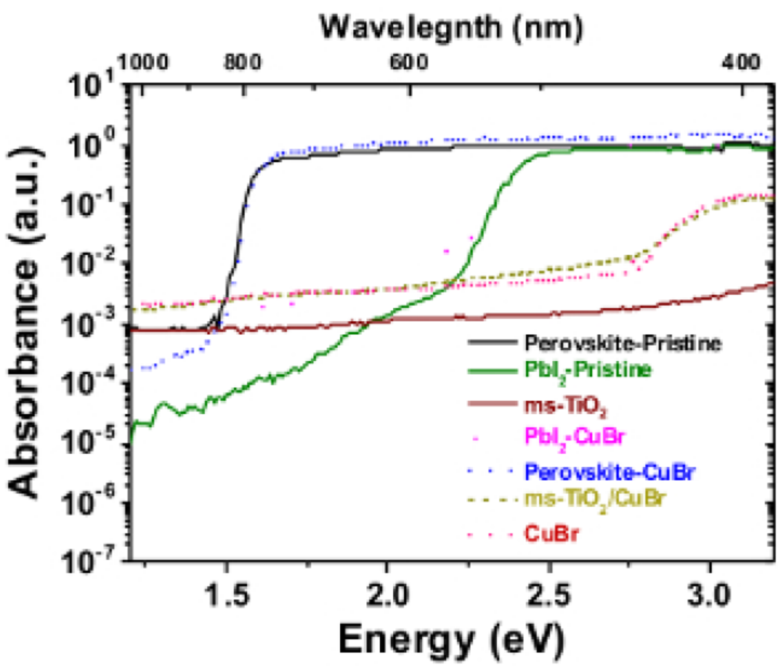
Effective mass

Energy level of trap states

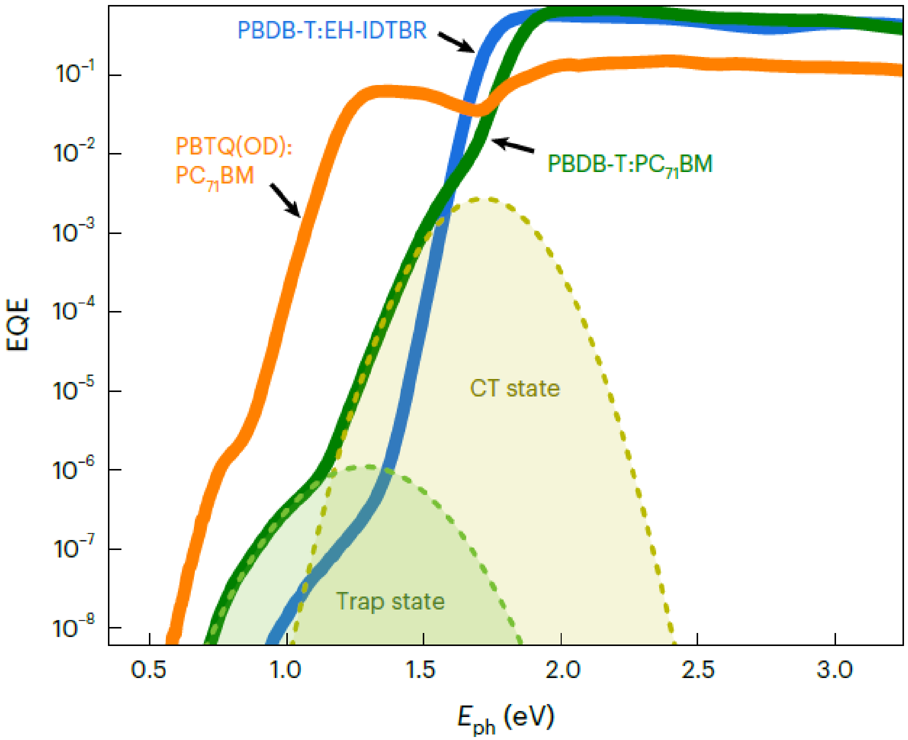
A. Saeki* *et al.*, ***J. Phys. Chem Lett***., 12: 1726-1733 (2021).

## Shallow trap states

Photothermal deflection spectroscopy (PDS)



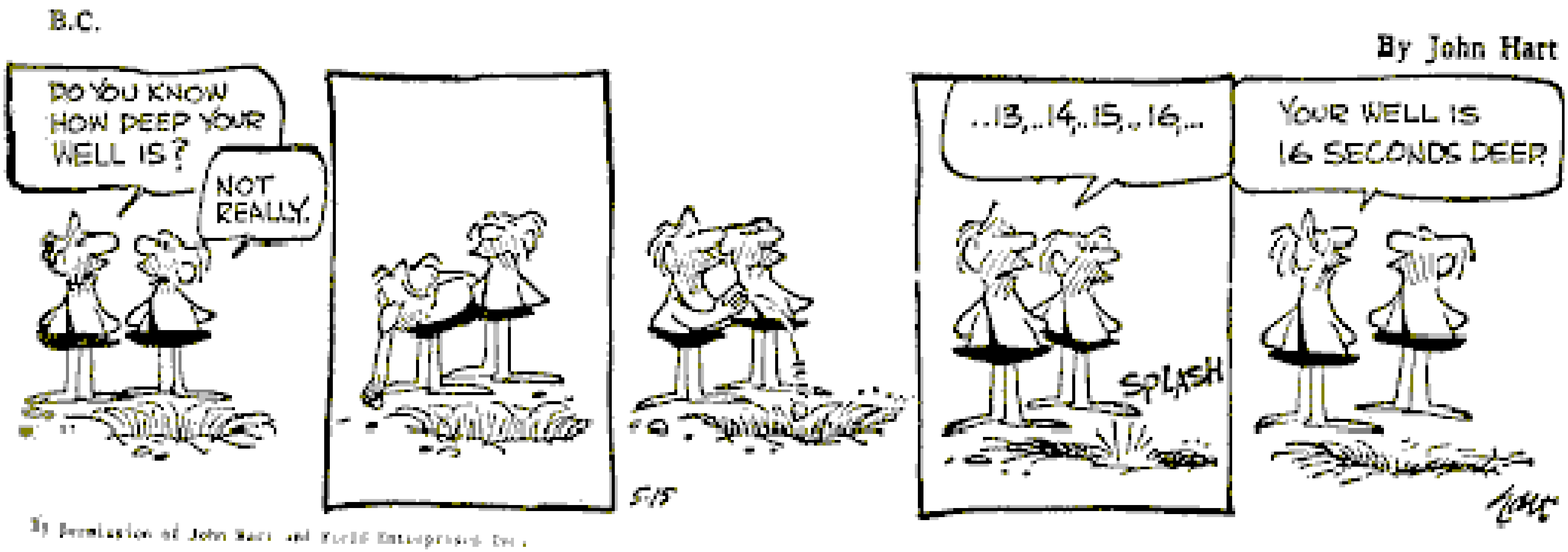

Sensitive-EQE




Abdi-Jalebi, M., *et al.*, ***Adv. Energy Mater***. 6: 1502472 (2016).

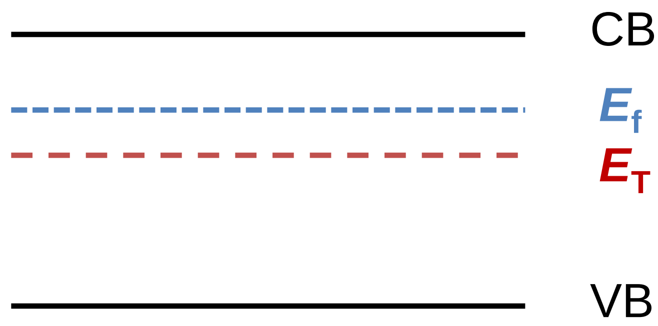
*Oskar J. Sandberg, Ardalan Armin et al.*, ***Nat. Photonics***. Doi.org/10.1038/s41566-023-01173-5 (2023).

# Pioneers in Measurements of Depth



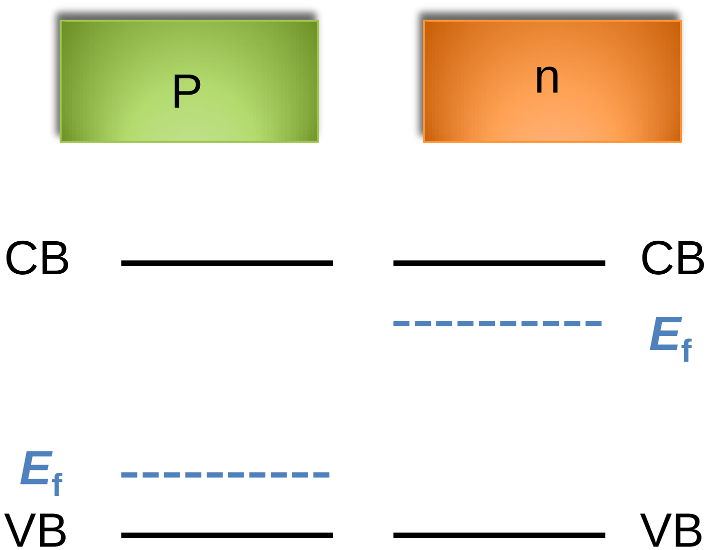

Serway, Raymond A., Beichner, Robert J. and Jewett, John W. **Physics for Scientists and Engineers** 5th Edition, Saunders College Publishing: Orlandon, FL, 2000

**Deep trap states (n-type: $E_T<E_f$)**

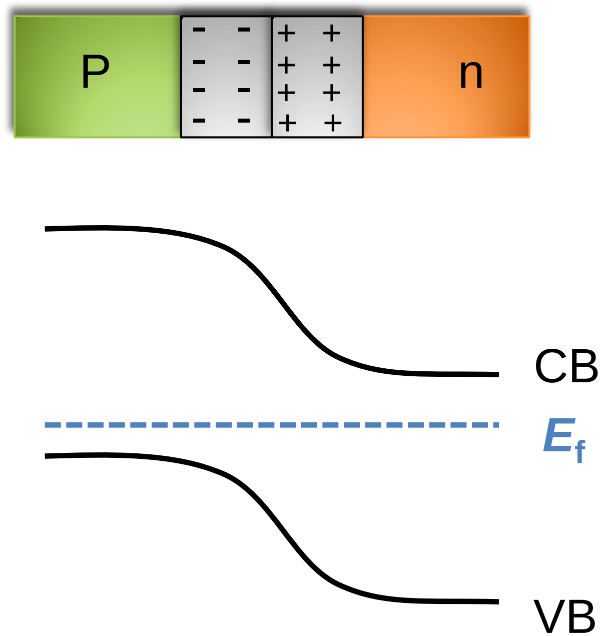



Junction capacitance

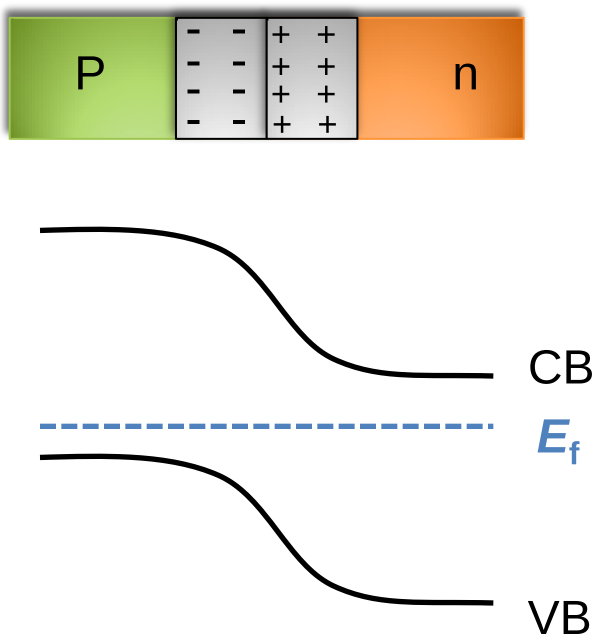
$$C=\frac{\varepsilon A}{W}$$



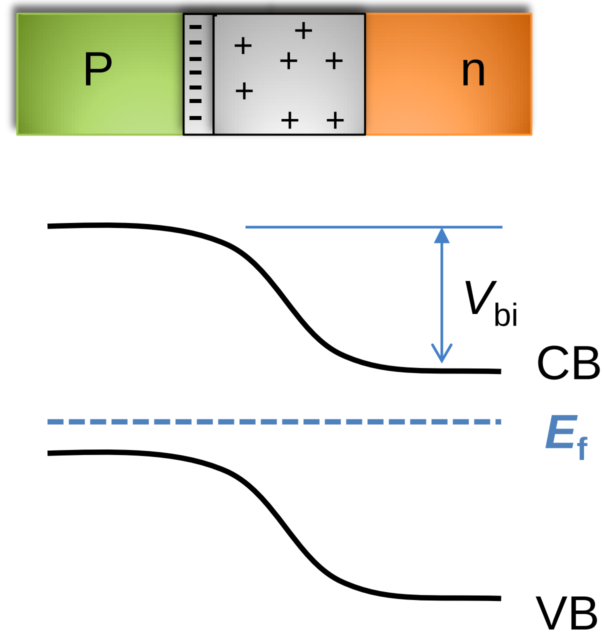

Space charge region
(**high resistance**、minor carriers)



Normal PN junction




P⁺N junction (W of p-region is very narrow)




$$W = \sqrt{\frac{2\varepsilon(V_{bi}+V)}{qn}}$$

Depletion width:

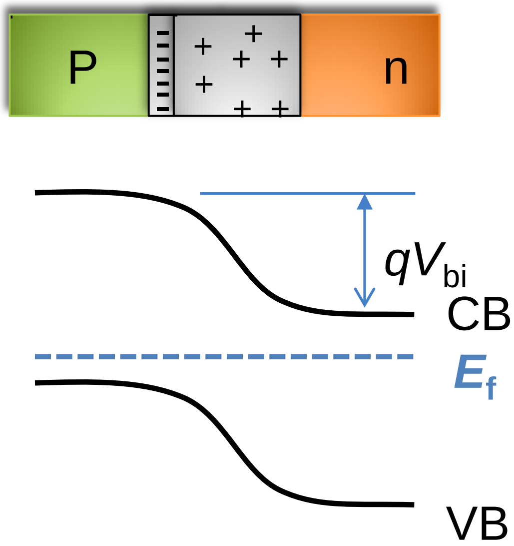
The higher concentration,

the narrower depletion width.

- *C*-*V* measurement

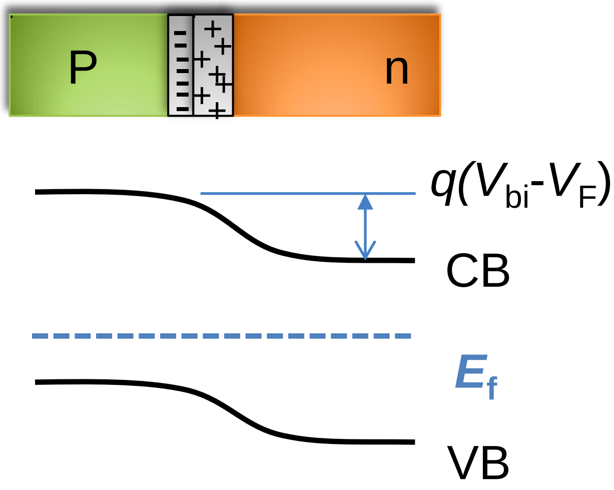
**Equilibrium**

$P^+N$ junction



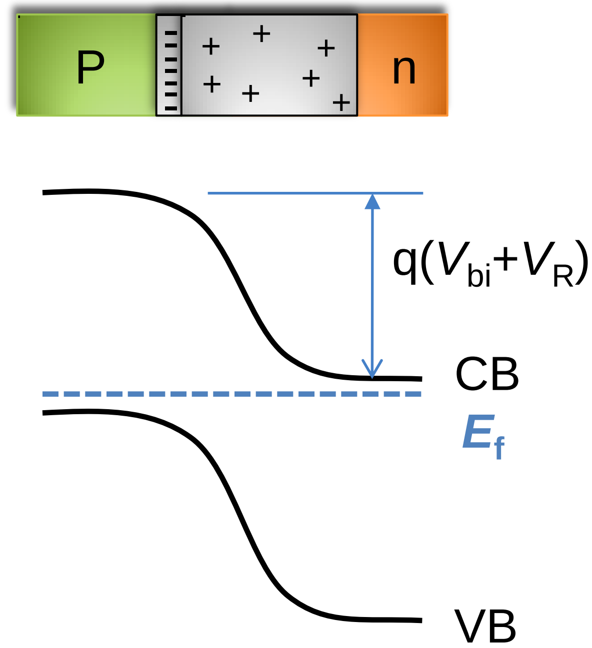

**Forward Bias**

$P^+N$ junction




**Reverse Bias**

$P^+N$ junction




$$C = \frac{\varepsilon A}{W}$$

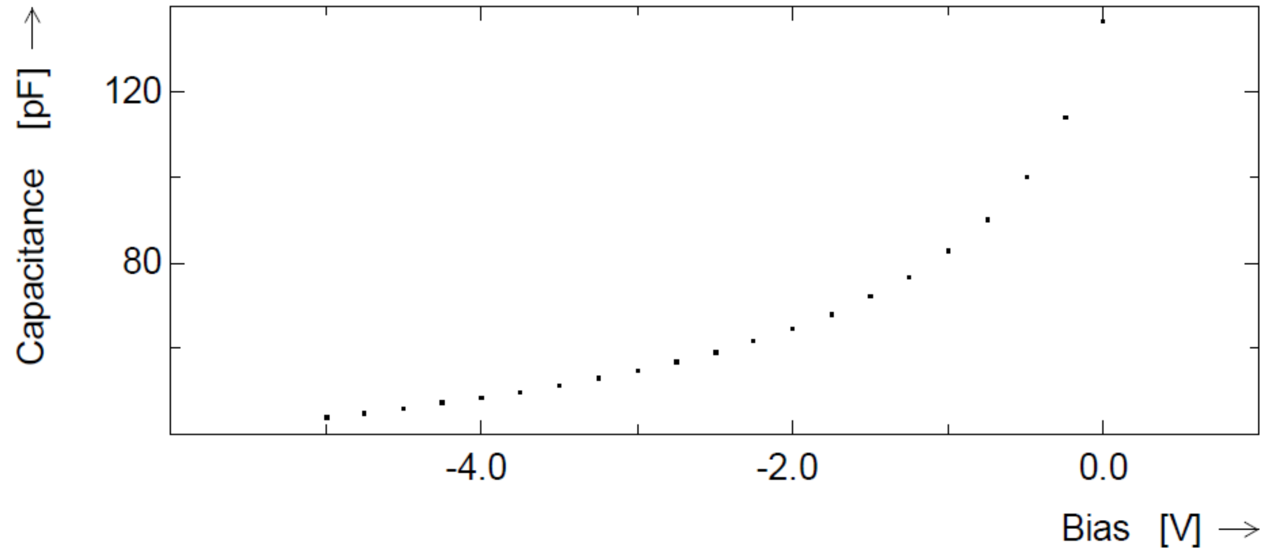
$$W = \sqrt{\frac{2\varepsilon(V_{bi}+V)}{qn}}$$

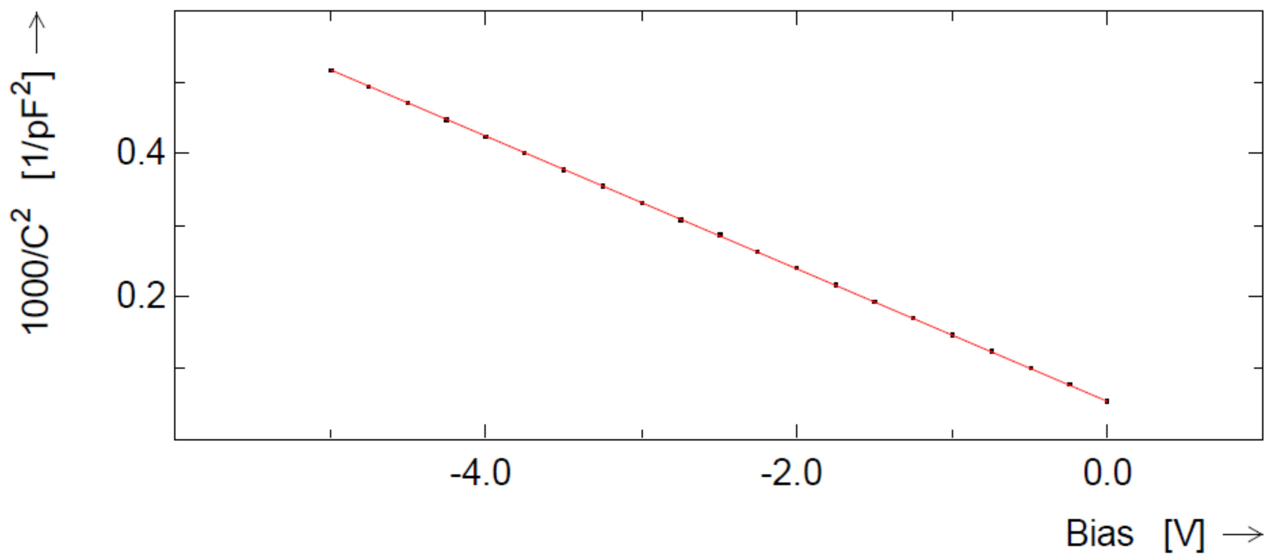
$$C = A\sqrt{\frac{\varepsilon qn}{2(V_{bi}+V)}}$$

$$\frac{1}{C^2} = \frac{2}{A^2\varepsilon qn}(V_{bi}+V)$$

$$E_c\text{-}E_F = k_B T ln(\frac{N_c}{n})$$

$$q\varphi_B = qV_{bi} + (E_c\text{-}E_F)$$




Name = @A_001.KCA
Comm = Standard
ID = TestID
rcID = 1001
Date = 2010-07-29
Type = n-Si
Area = 8.00E-03 $cm^2$
Temp = 270.15 K
$N_S$ = 2.00E+15 $cm^{-3}$
$U_D$ = -0.581 V
$phi_B$ = 0.800 eV
Correl = 1.00000

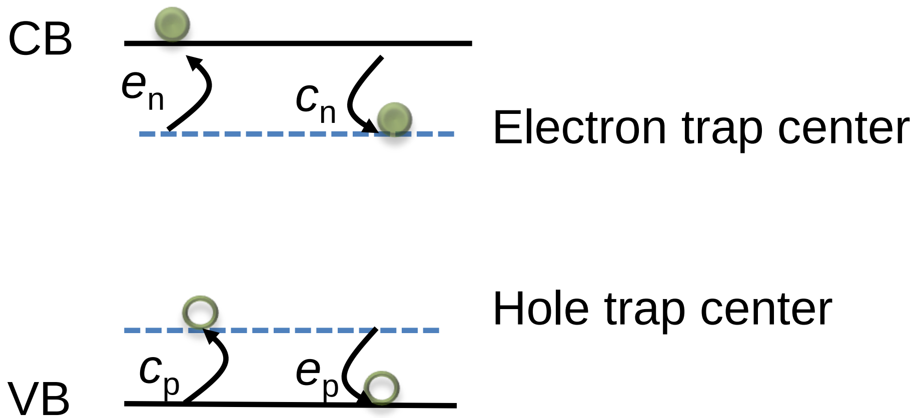
**There are traps within the space charge region!**

Thermal (electron) emission rate:

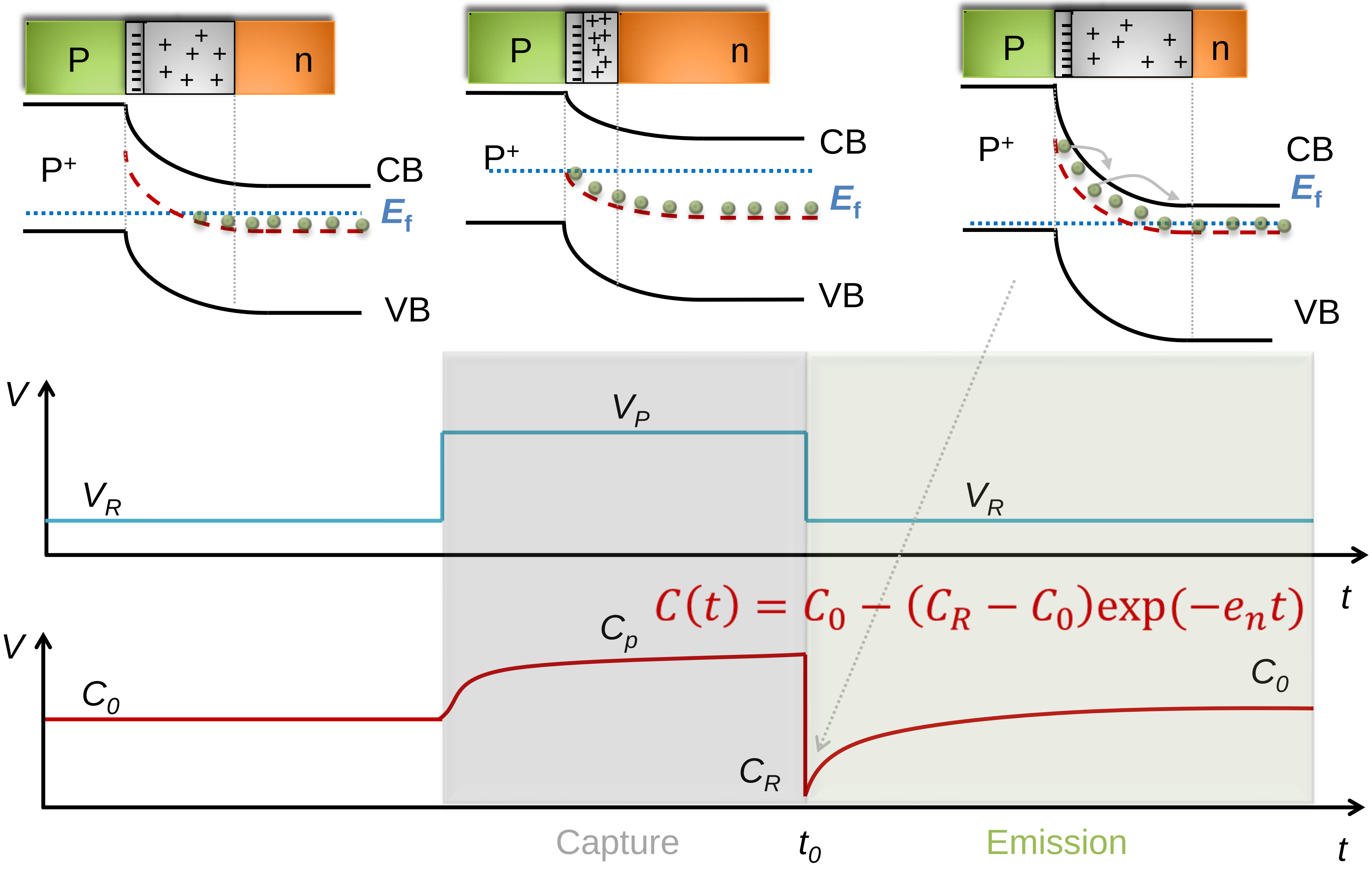
$$e_n = \frac{\sigma_n v_n N_c}{g} \exp\left( \frac{-(E_C - E_t)}{kT} \right)$$

$$v_n \propto T^{\frac{1}{2}} \qquad N_c \propto T^{\frac{3}{2}}$$

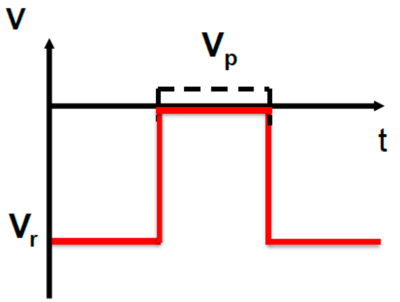
$$e_n = \sigma_n \beta T^2 \exp\left( -\frac{E_C - E_t}{kT} \right)$$



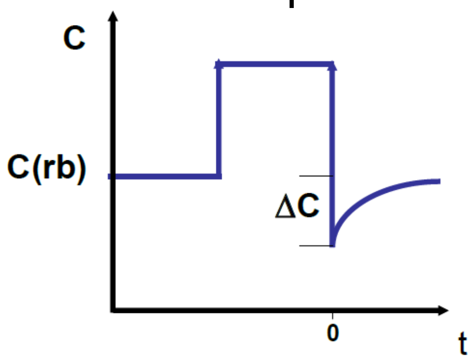
## Transient capacitance

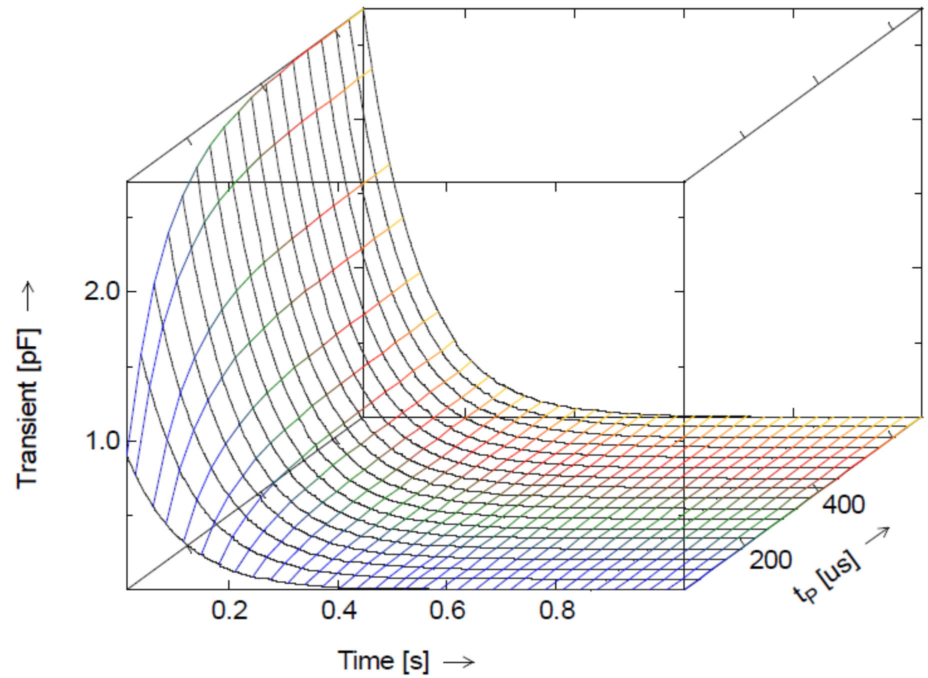


Optical pulse can also inject carriers within the SCR

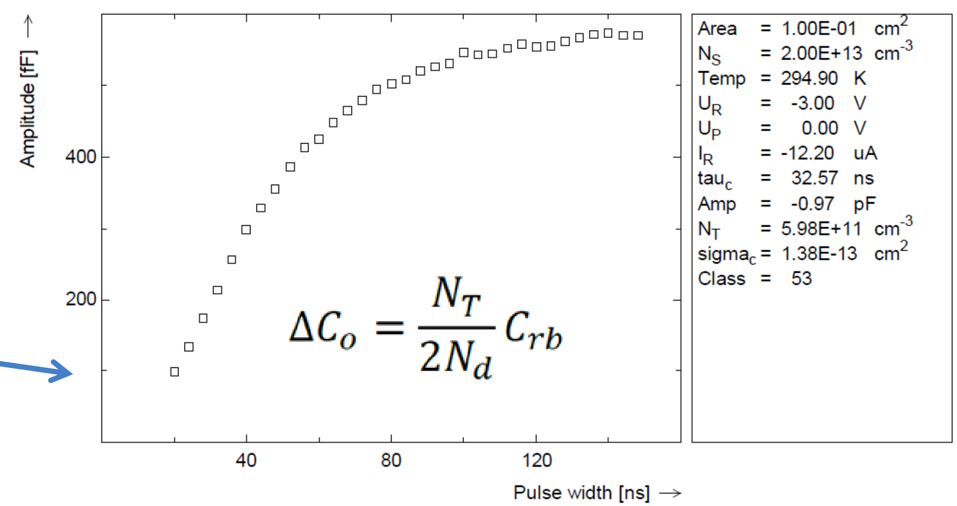



Bias pulse




Trap concentration can be obtained from the maximum amplitude of the DLTS transient



- **Principle of DLTS**

Thermal (electron) emission rate:

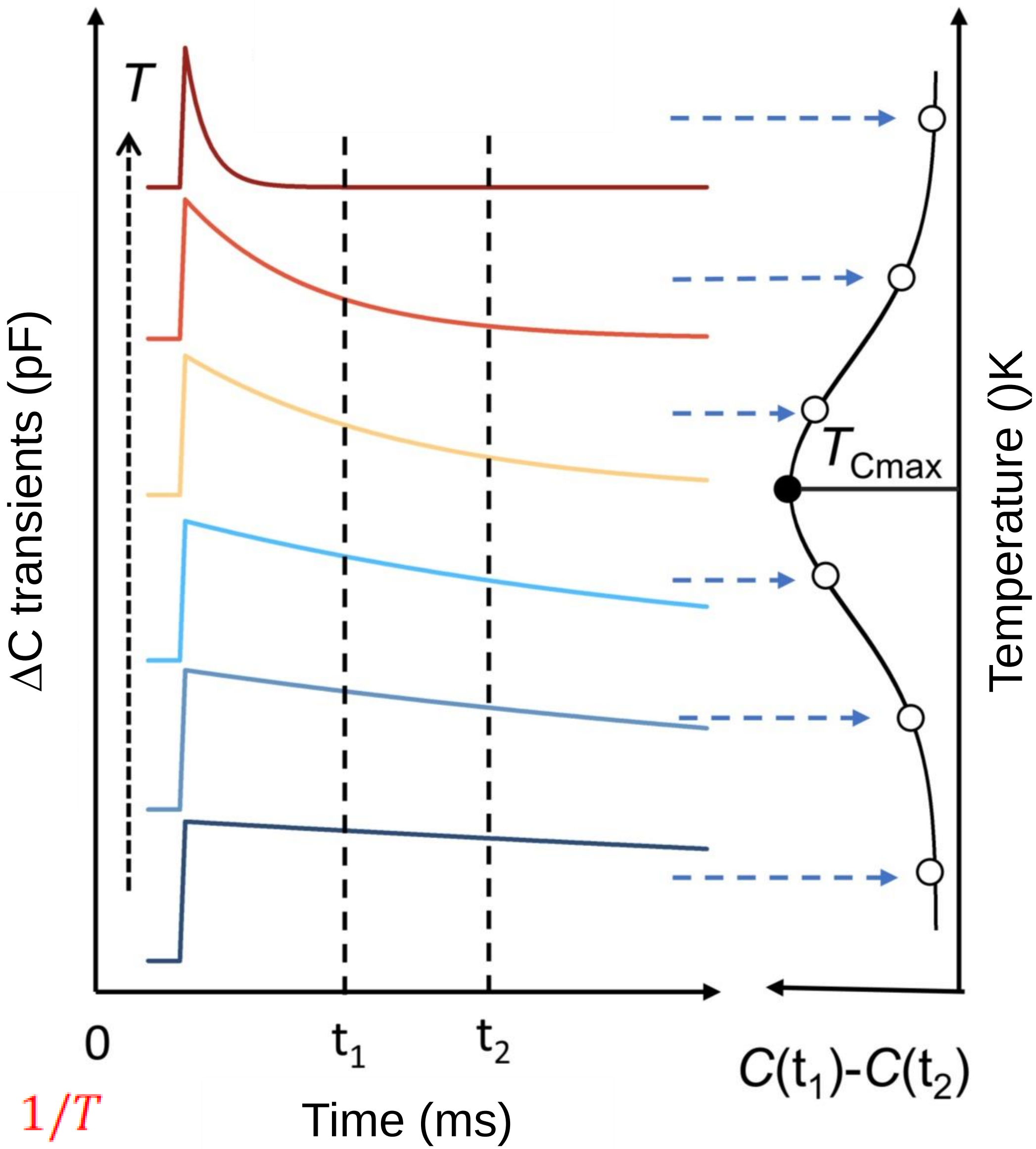
$$e_n = \frac{\sigma_n v_n N_c}{g} \exp\left(\frac{-(E_C - E_t)}{kT}\right)$$

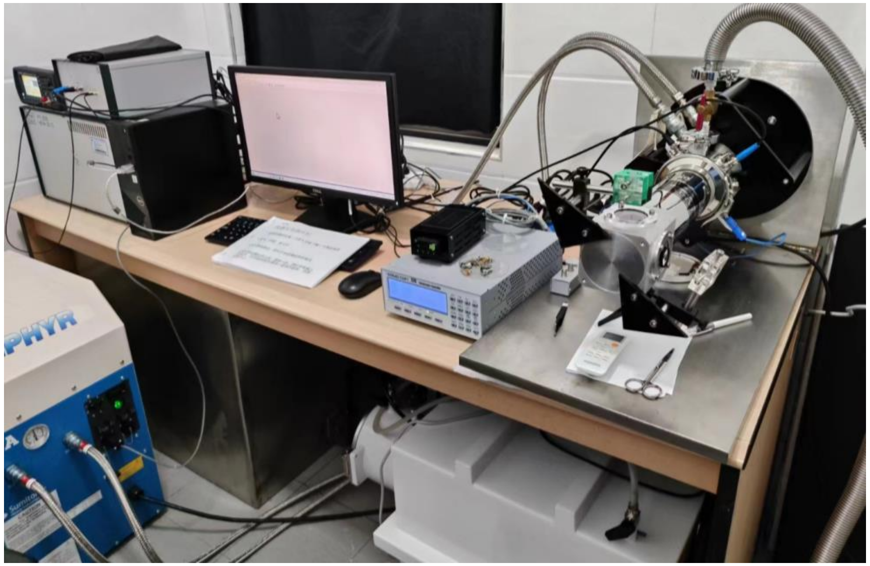
$$v_n \propto T^{\frac{1}{2}} \qquad N_c \propto T^{\frac{3}{2}}$$

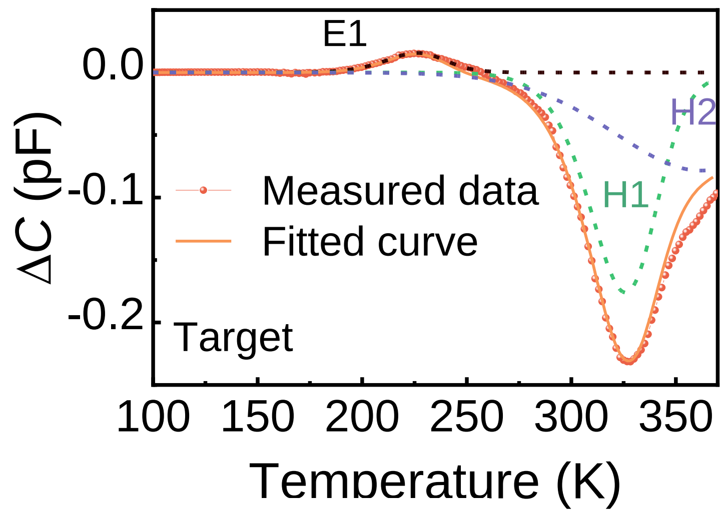
$$e_n = \sigma_n \beta T^2 \exp\left(-\frac{E_C - E_t}{kT}\right)$$

$$ln\left[\frac{e_n}{T^2}\right] = ln\,(\beta\sigma_n) - \frac{E_c - E_T}{kT}$$

Arrhenius plot of $ln\left[\frac{e_n}{T^2}\right]$ against $1/T$

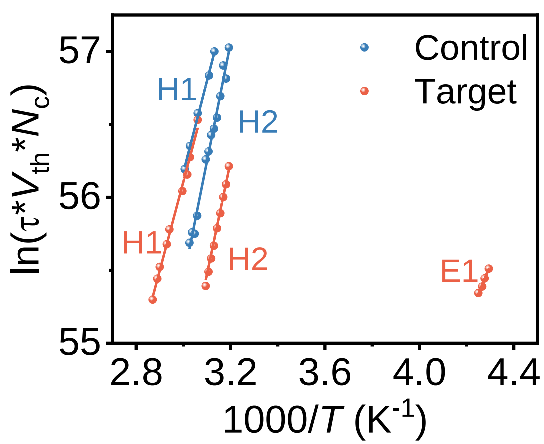


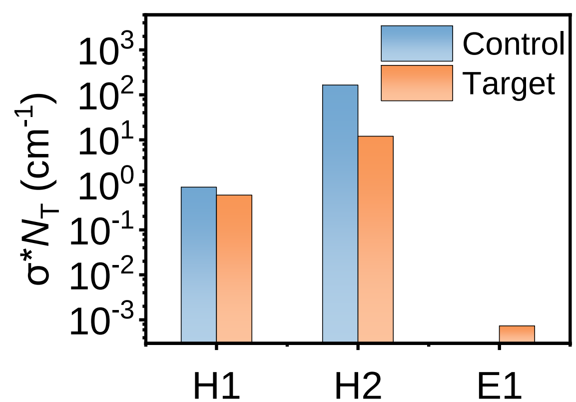





Arrhenius plot of $ln\left[\frac{e_n}{T^2}\right]$ against $1/T$

$$ln\left[\frac{e_n}{T^2}\right] = ln\,(\beta\sigma_n) - \frac{E_c - E_T}{kT}$$

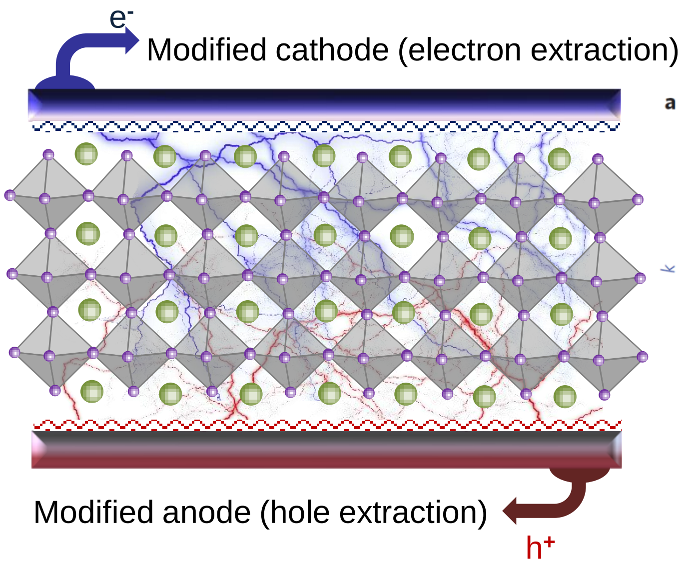


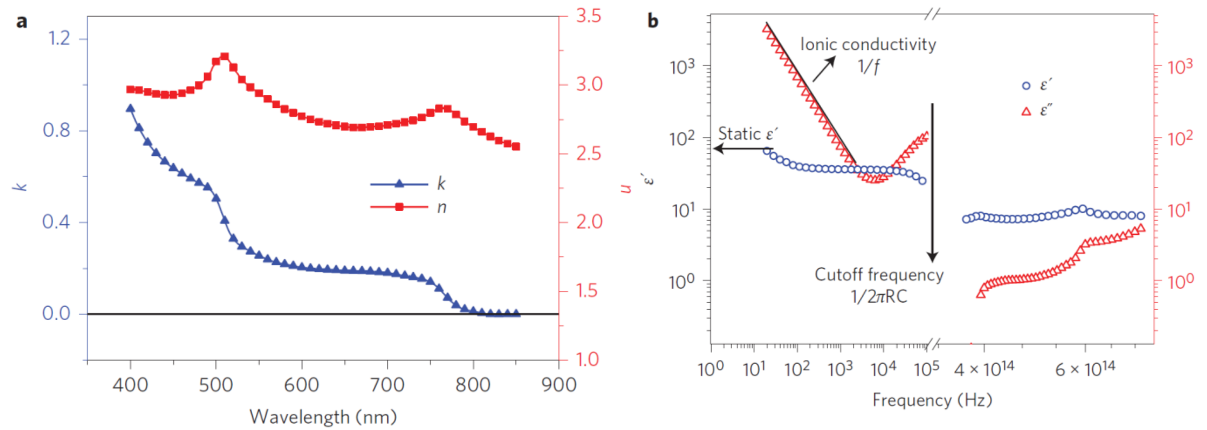



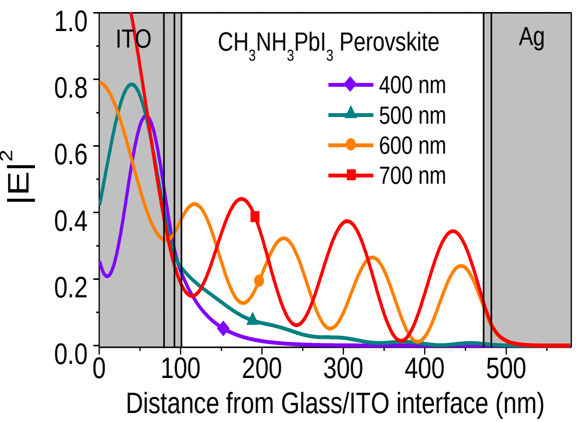

Q. Lin* *et al*. Appl. Phys. Rev. 9, 0211405 (2022)
Q. Lin* *et al*. Appl. Phys. Lett. 120, 221102 (2022)

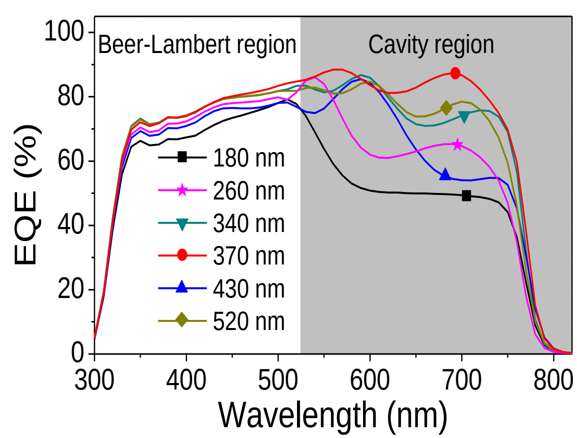
- **Perovskite solar cells: strategies to boost the PCE**

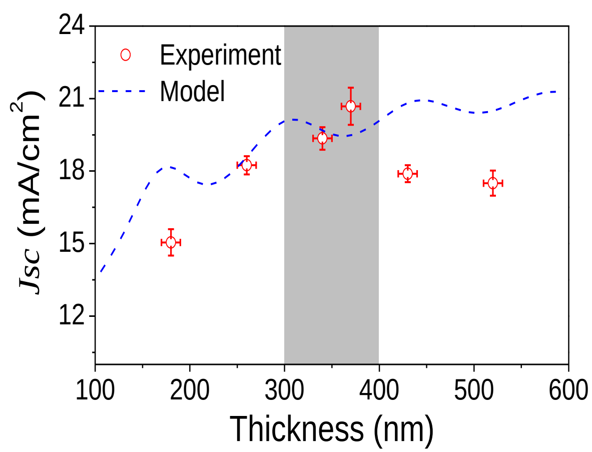
**1. Optical cavity optimization → $J_{sc}$**



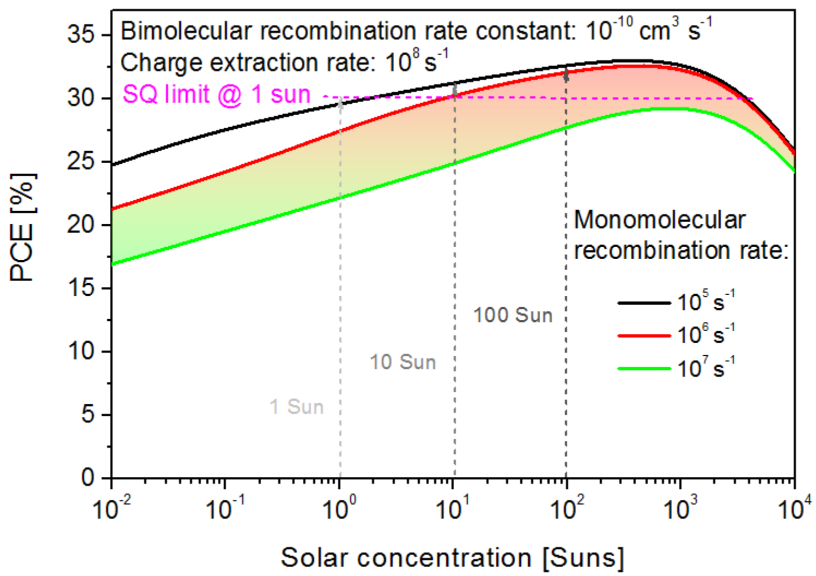



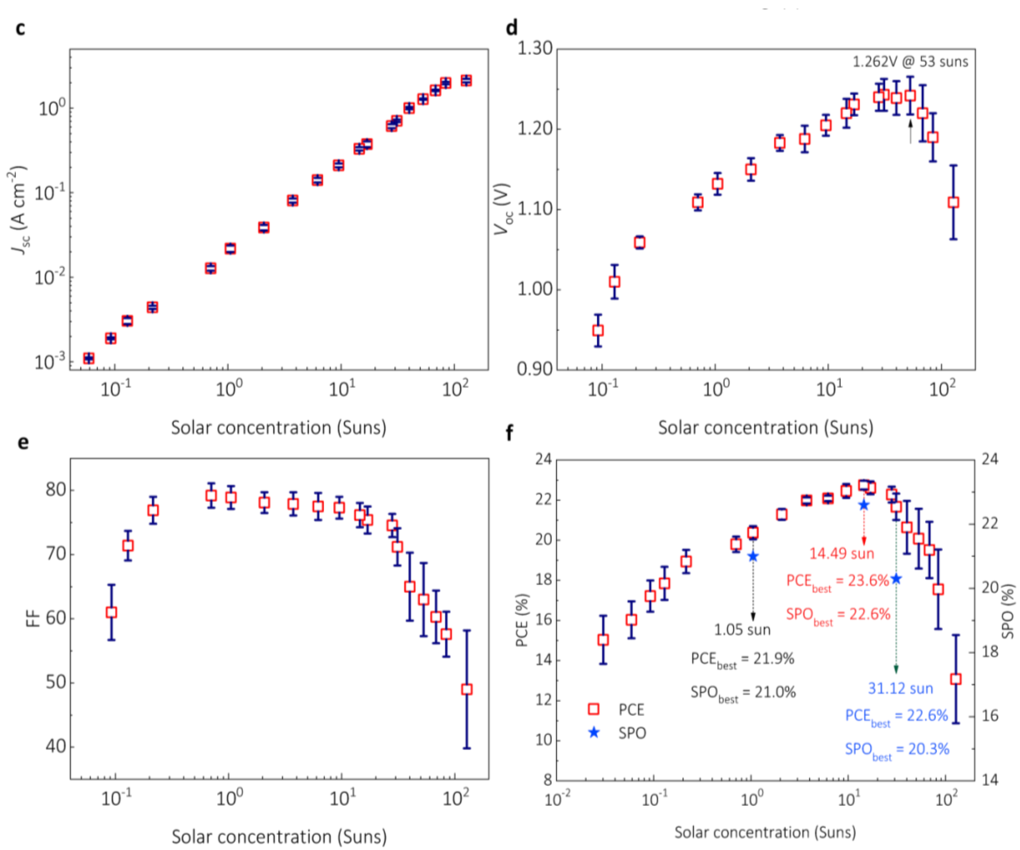




**Q. Lin**, A. Armin, R. Nagiri, P. Burn*, P. Meredith*,, **Nature Photon.** 9 (2015) 106-112.

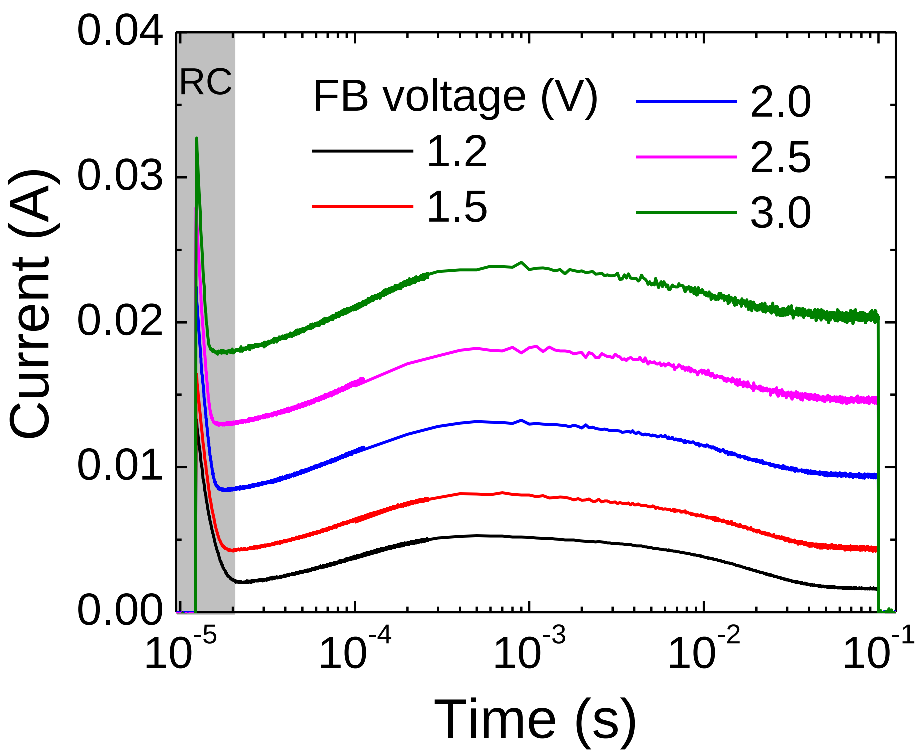


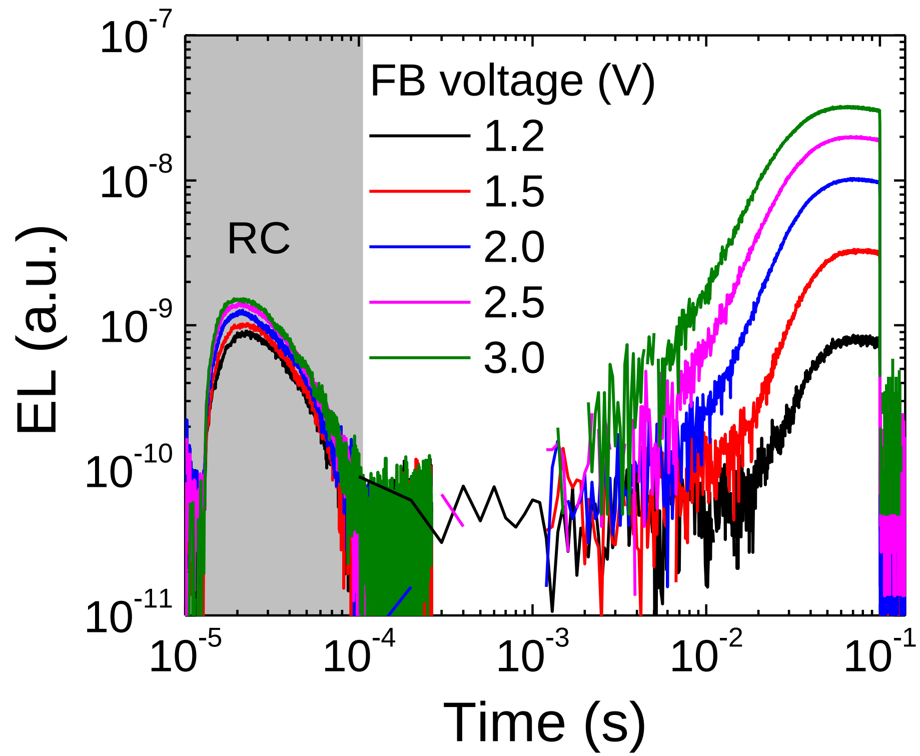




**Q. Lin**, Z. Wang, H. J. Snaith, M. B. Johnston, L. M. Herz* et al., *Adv. Sci.* **5** (2018), 1700792

Z. Wang#, **Q. Lin#**, L. M. Herz, H. J. Snaith* *et al.*, *Nature Energy*, **3** (2018), 855-861

## Light emitting diodes

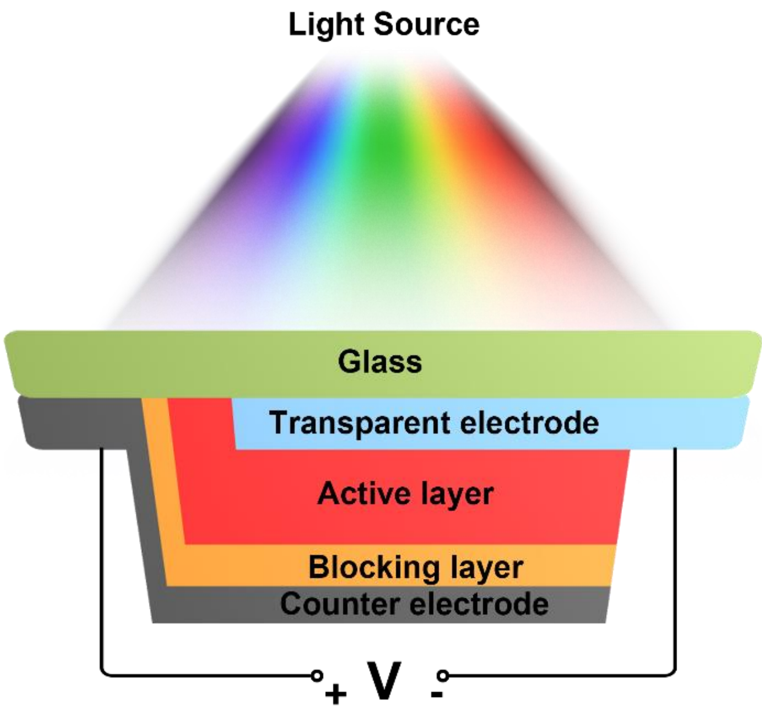


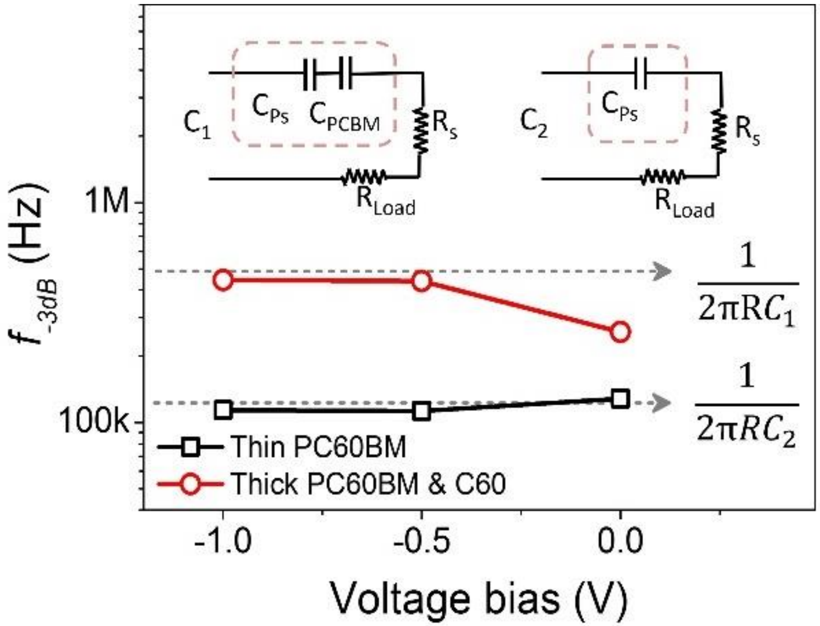




Evaluation of ion migration within perovskites via double injection and transient EL

Q. Lin, *et al*., unpublished work.

Jia Yang, Wangping Sheng, Ruiming Li, Lingyun Gong, Yanyan Li, Licheng Tan*, **Qianqian Lin***, Yiwang Chen*. Uncovering the mechanism of poly(ionic-liquid)s multiple inhibition of ion migration for efficient and stable perovskite solar cells. ***Adv. Energy Mater***.,12: 2103652 (2022).




$$f_{RC} = \frac{1}{2\pi RC} \qquad C = \varepsilon_0 \varepsilon_r \frac{A}{d}$$

$$\frac{1}{f_{-3dB}^2} = \frac{1}{f_t^2} + \frac{1}{f_{RC}^2}$$

**Q. Lin** *et al*., **Adv. Mater.,** 27**:** 2060-2064 (2015) .

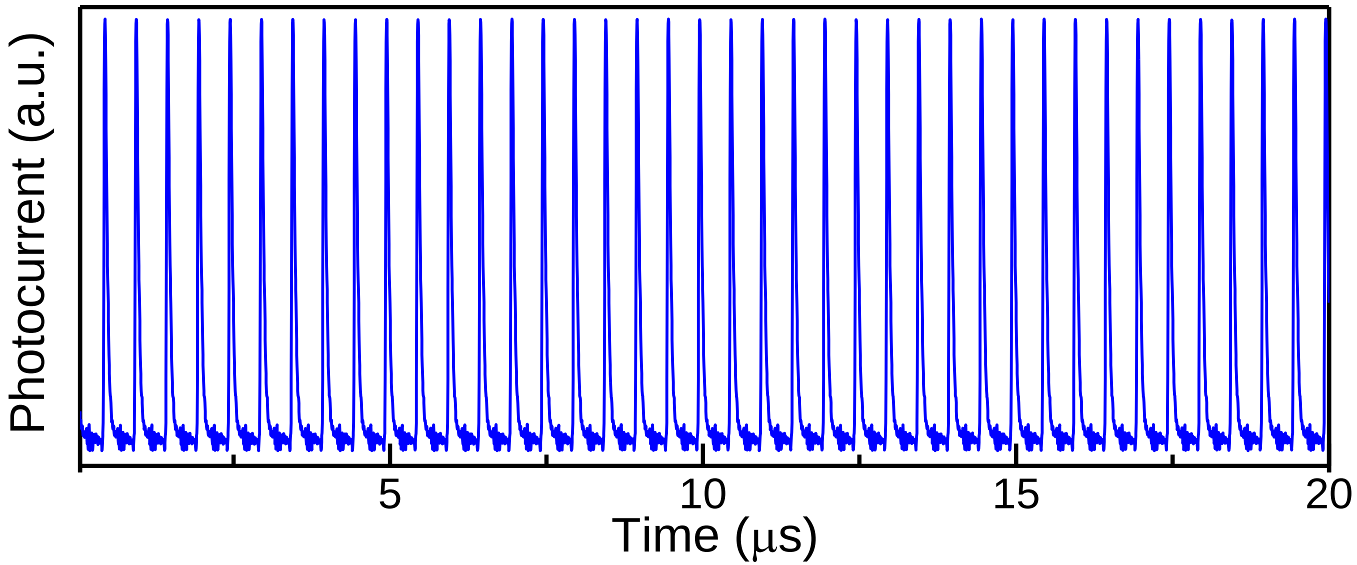
**Q. Lin** *et al.*, ***Nat. Photonics***, **9**: 687–694 (2015), .

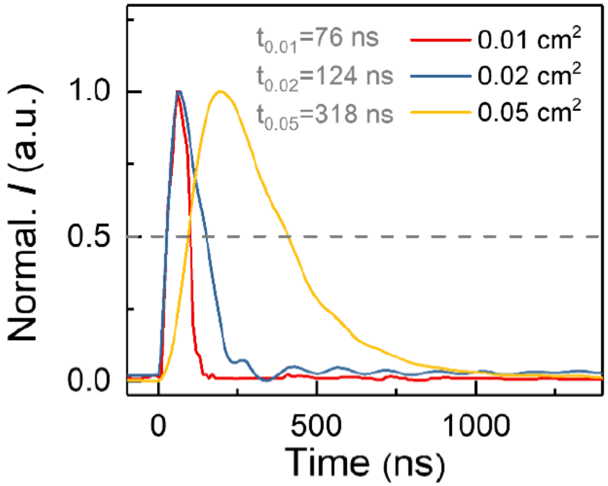
**Q. Lin** *et al.*, **Adv. Funct. Mater.** 27: 1702485 (2017).

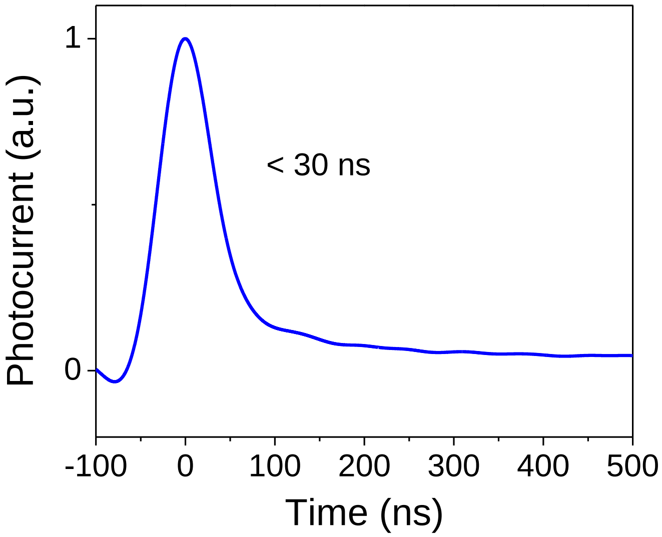
W. Li, L. Ding*, **Q. Lin*** *et al.*, **Adv. Funct. Mater.** 29: 1808948 (2019).

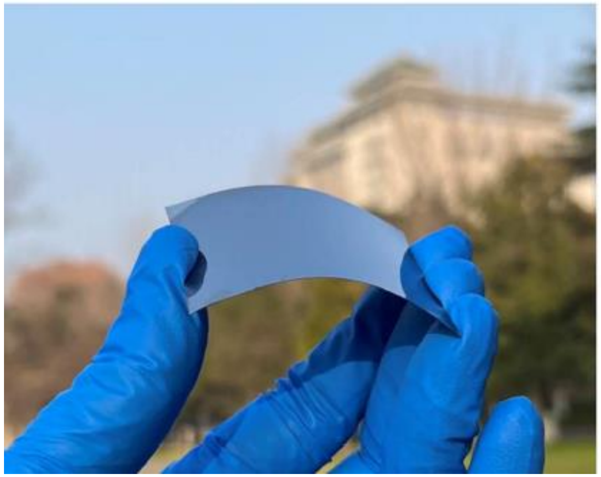
Y. Xu, **Q. Lin*** *et al.*, **Adv. Funct. Mater.** 33: 2212523 (2023).

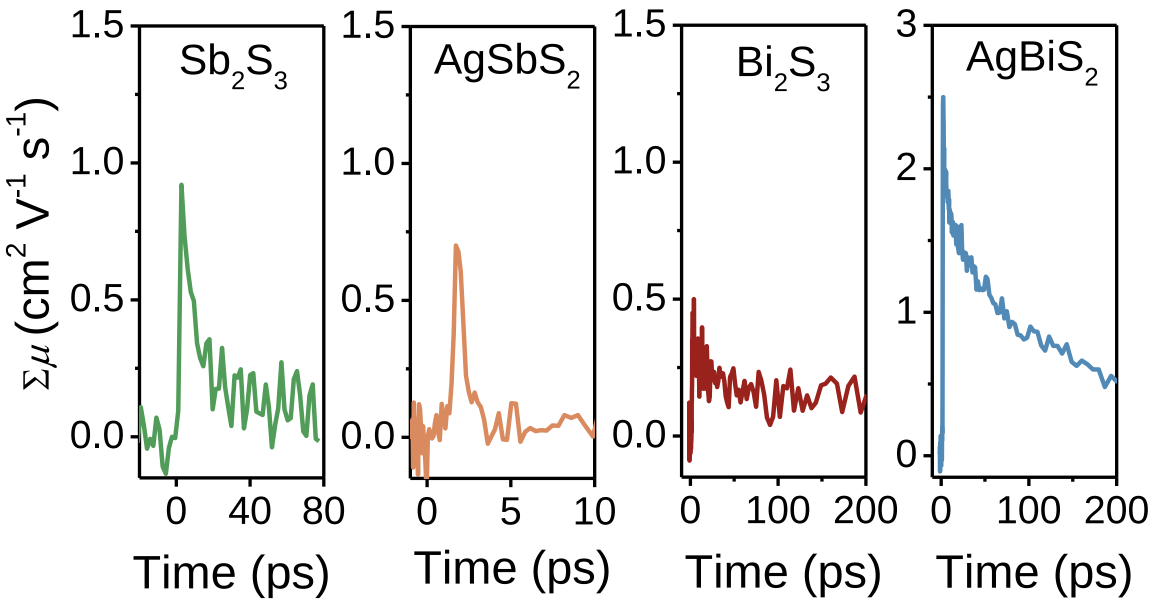
# Is GHz bandwidth possible?

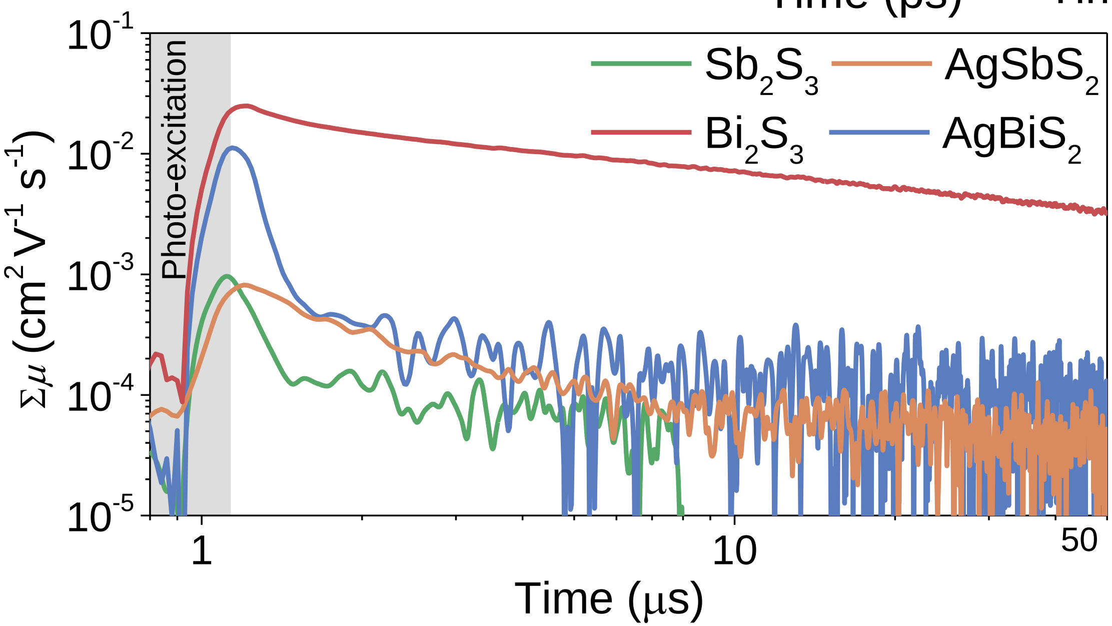






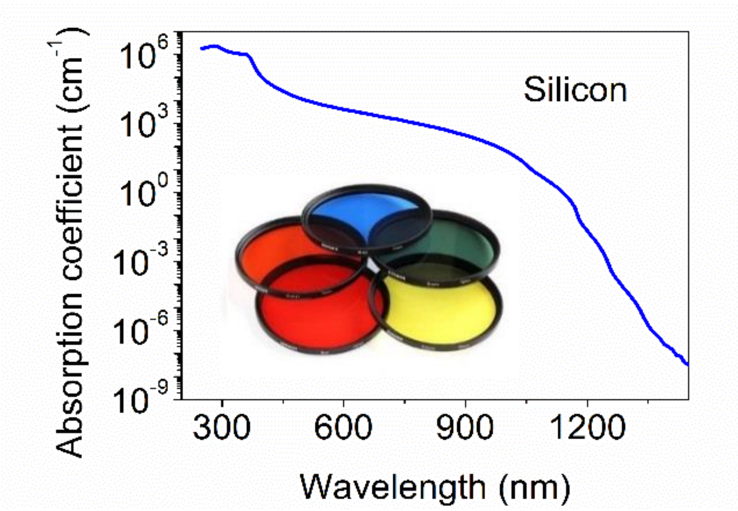




$$t_{tr} = \frac{d^2}{\mu * (V_{bi} - V_{bias})}$$

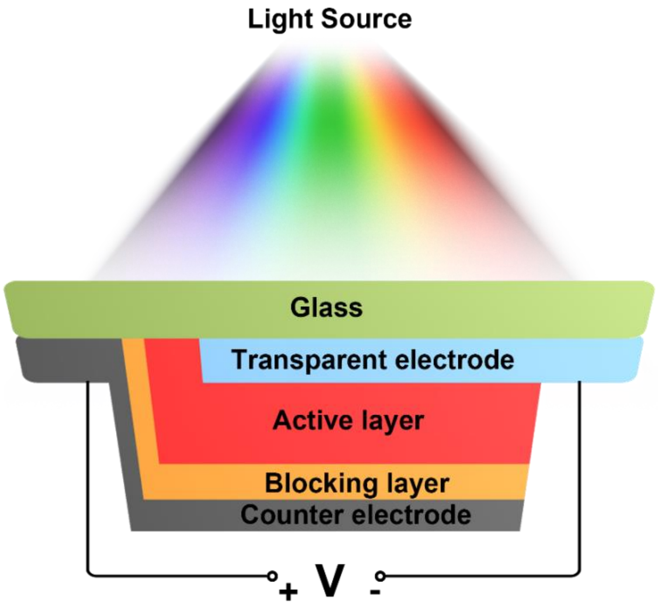
$$f_t = \frac{3.5}{2\pi t_{tr}}$$

Z. Jia, H. Laura*, Q. Lin*, *et al.*, ***ACS Energy Lett.,*** 8: 1485-1492 (2023).

**Filterless Photodetectors**

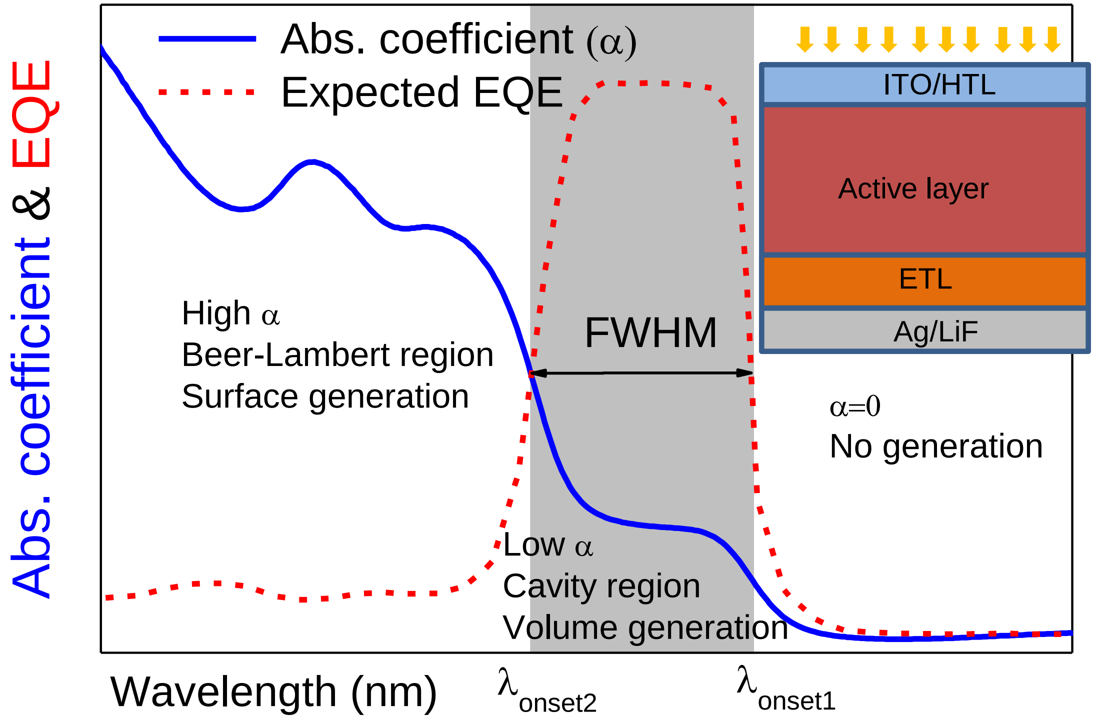



~10 million pixels
1.8 × 2.7 cm
~5 μm size
Filters

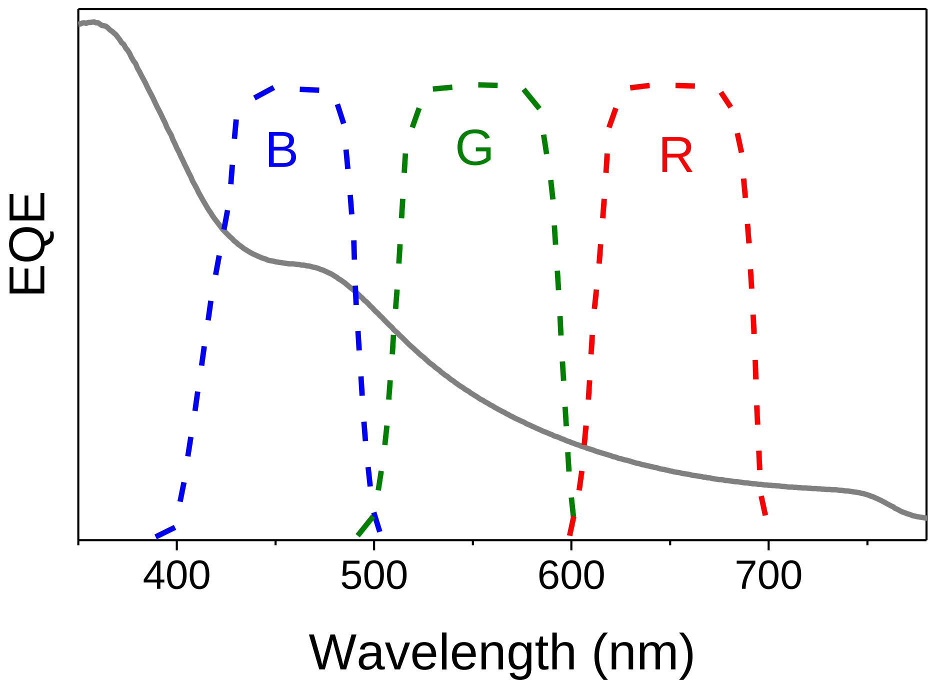



- ✓ Narrowband absorbers;
- ✓ Splitting the input light
- ✓ Charge collection narrowing (CCN).

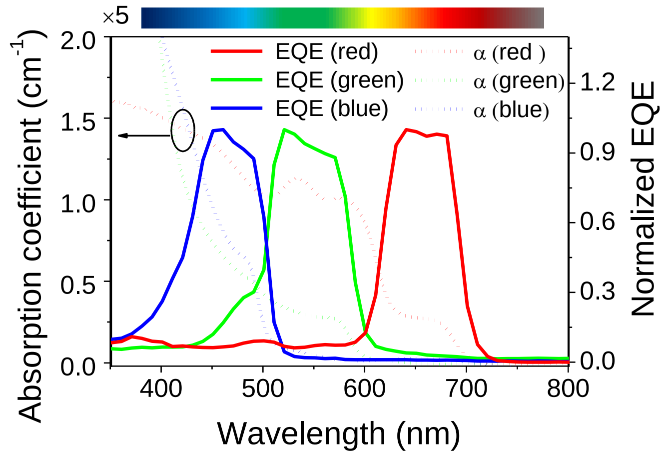
A. Armin *et al.*, *Nature Comm.* **6**: 6343 (2015).
Q. Lin *et al.*, *Nature Photon.* **9**: 687–694 (2015).

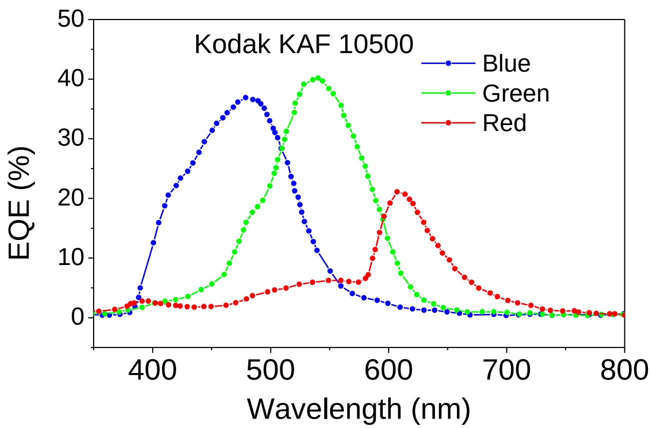



A. Armin *et al*., *Nature Comm.* **6**: 6343 (2015).
Q. Lin *et al*., *Nature Photon.* **9**: 687–694 (2015).

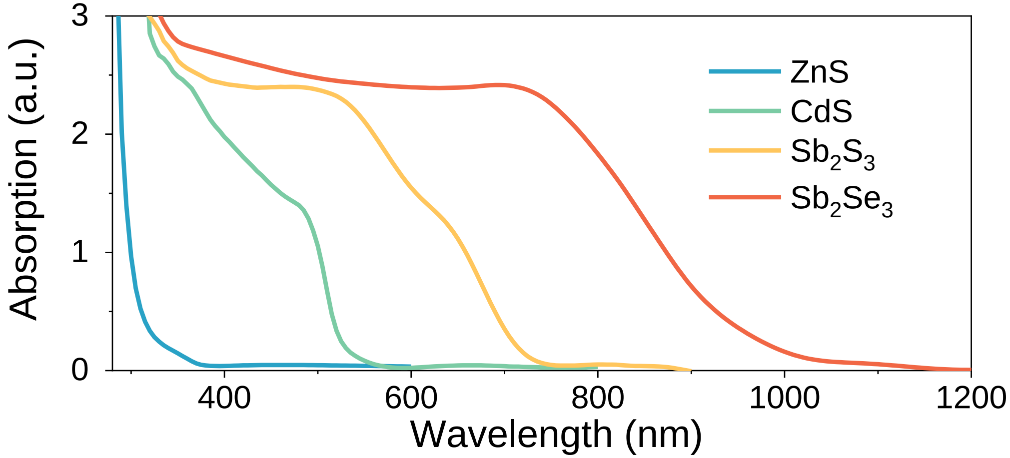


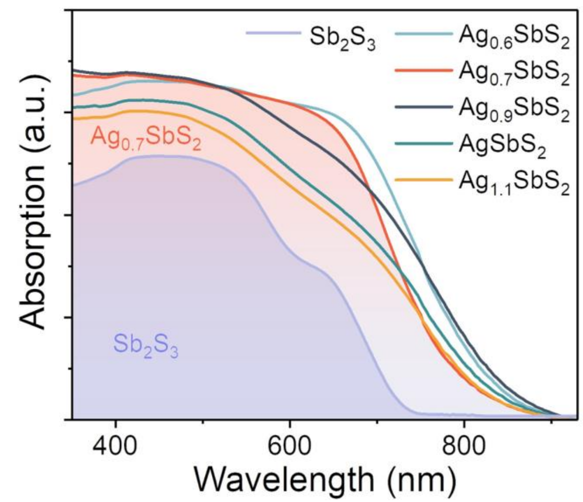

## Realization of RGB detectors

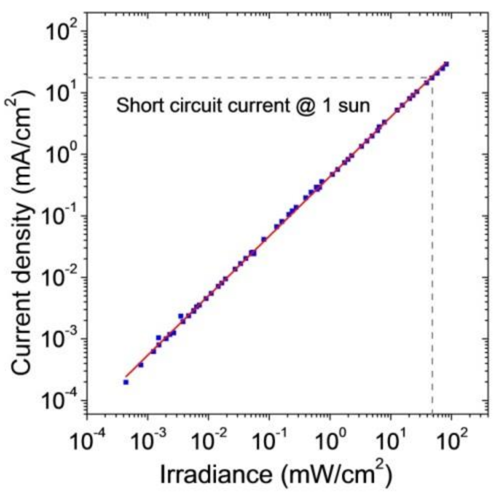



A. Armin *et al.*, *Nature Comm.* **6**: 6343 (2015).
Q. Lin *et al.*, *Nature Photon.* **9**: 687–694 (2015).



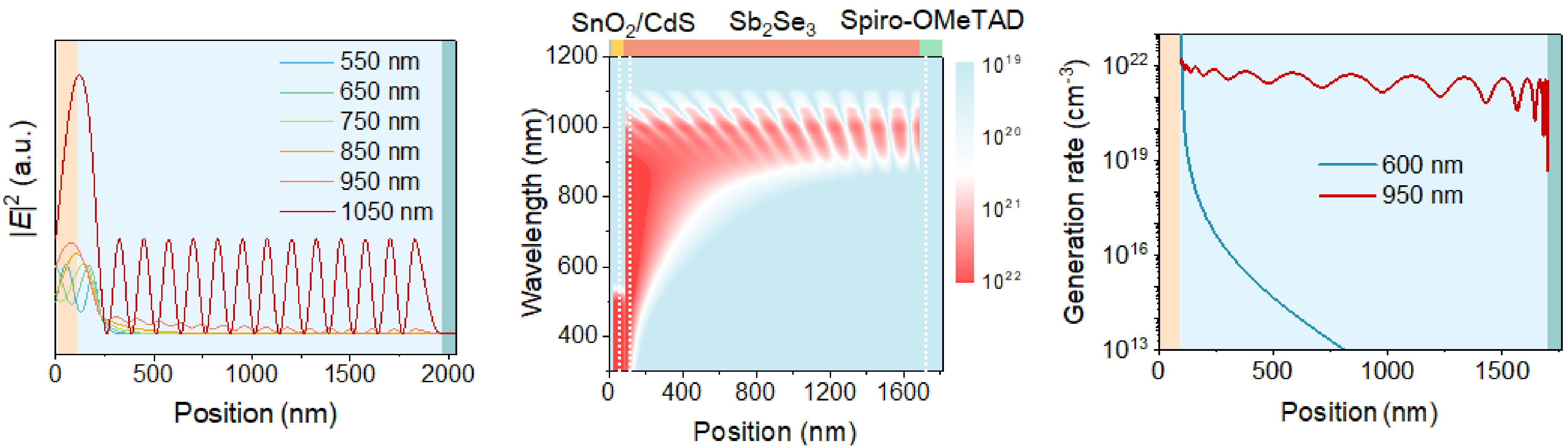




Tunable bandgap → Spectral bandwidth

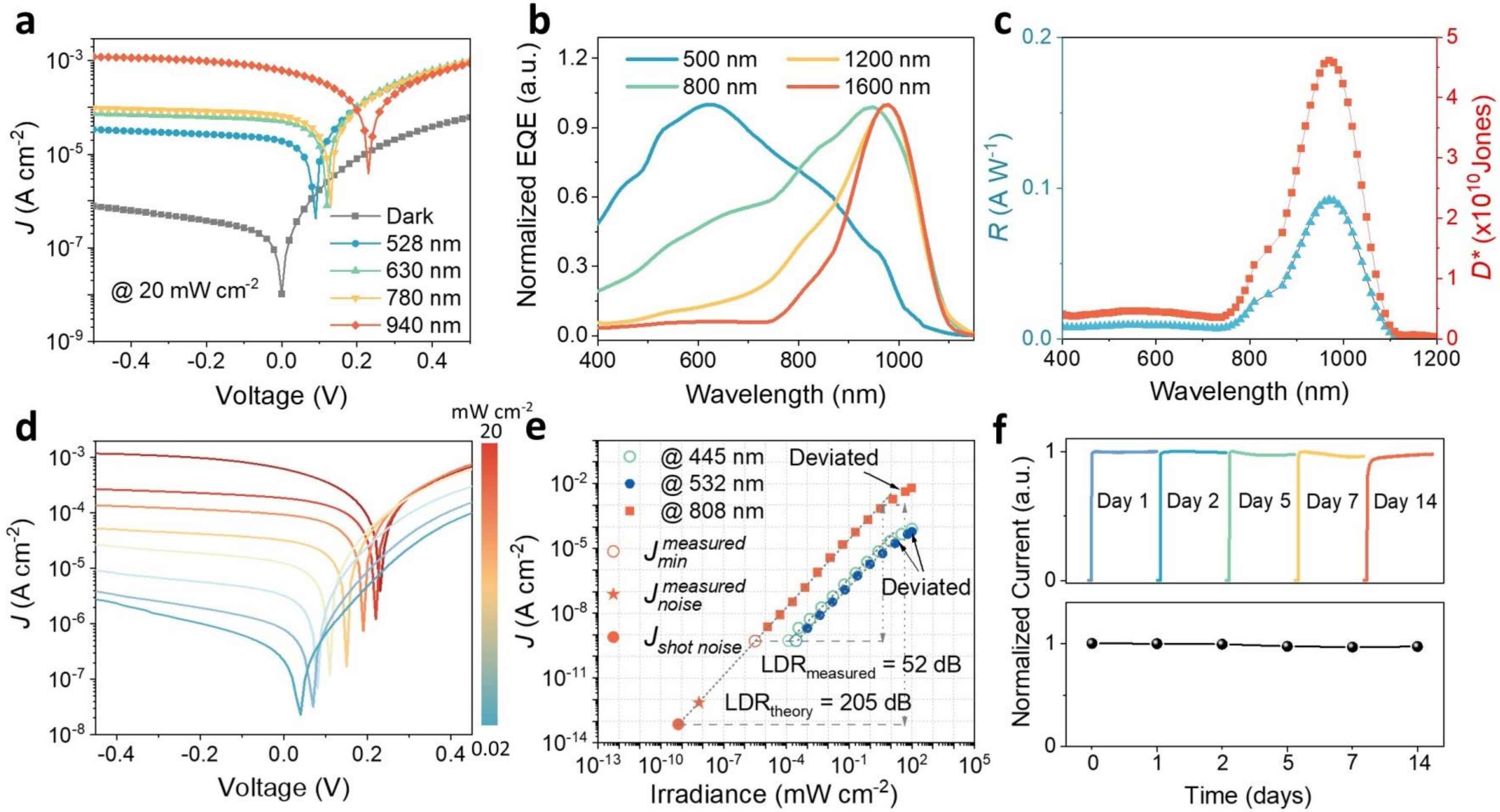
Low recombination → Large LDR

High mobility → Fast response

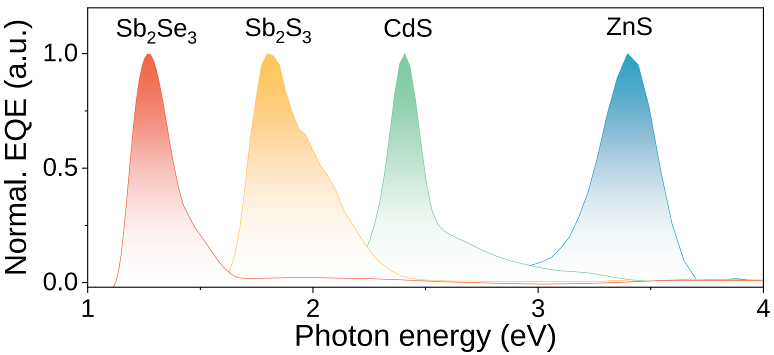


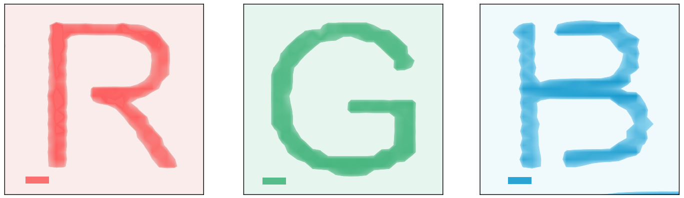

Y. Xu, **Q. Lin*** *et al.*, **Adv. Funct. Mater.** 33: 2212523 (2023).

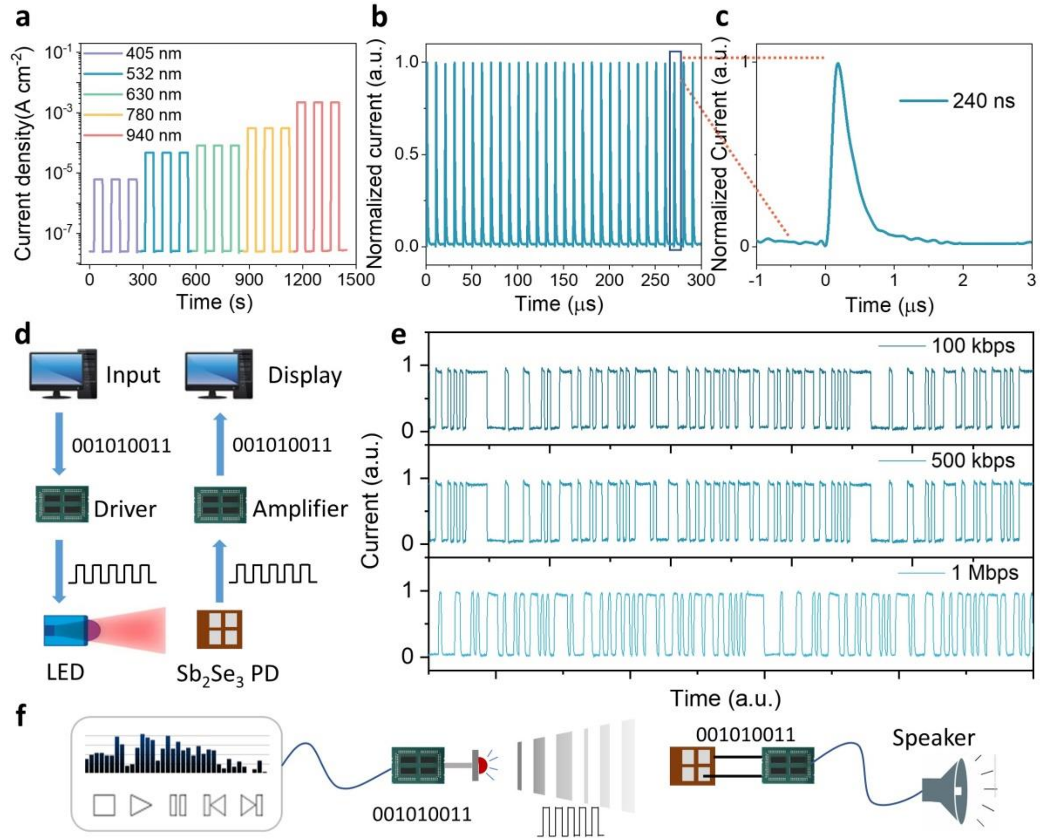
# Proof of concept




Y. Xu, **Q. Lin*** *et al.*, **Adv. Funct. Mater.** 33: 2212523 (2023).

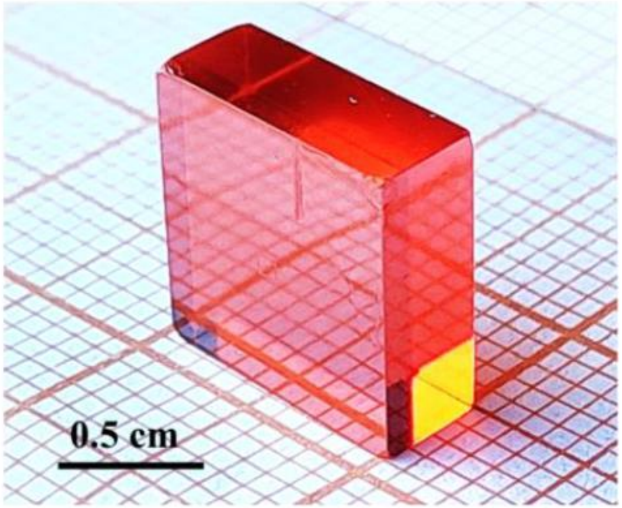


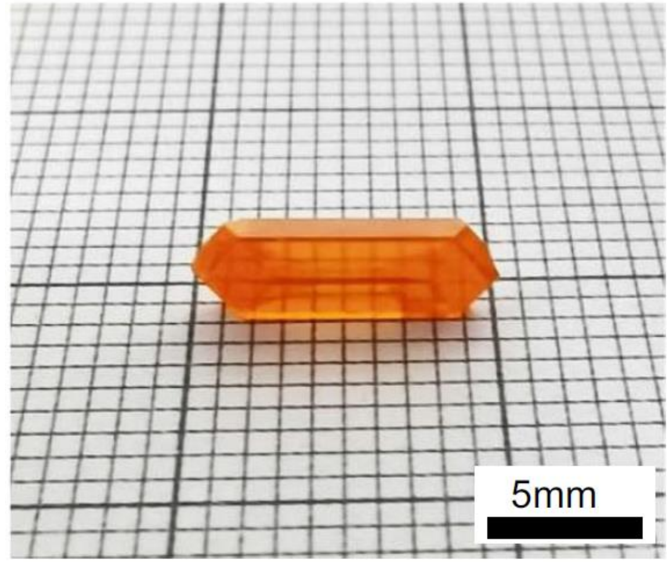



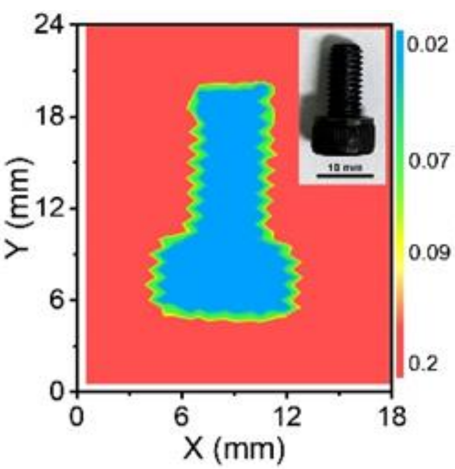


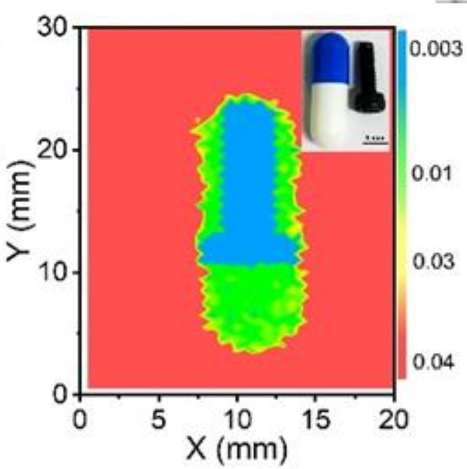

Y. Xu, **Q. Lin*** *et al.*, **Adv. Funct. Mater.** 33: 2212523 (2023).
R. Li, **Q. Lin*** *et al.*, **Adv. Funct. Mater.** 33: 2307005 (2023).

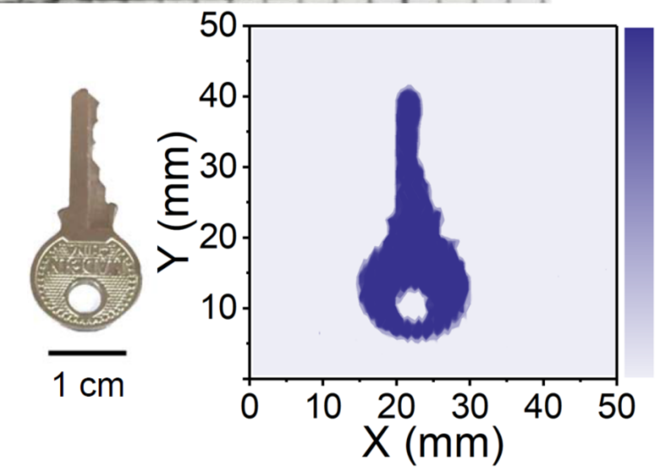
## Photodetection and Imaging 1



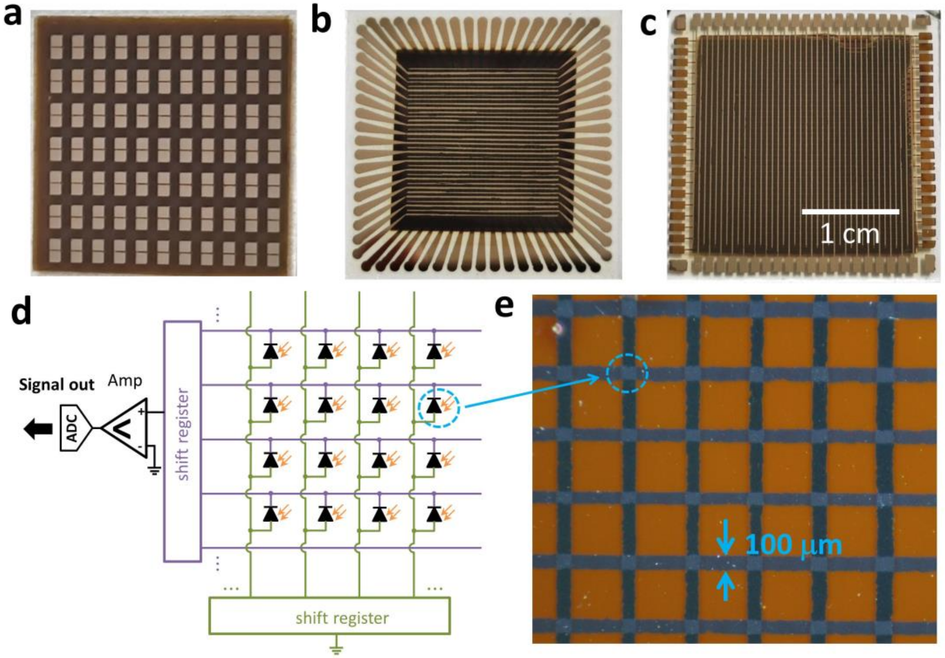




J. Peng, **Q. Lin*** *et al.*, ***Matter***, 5: 2251-2264 (2022).

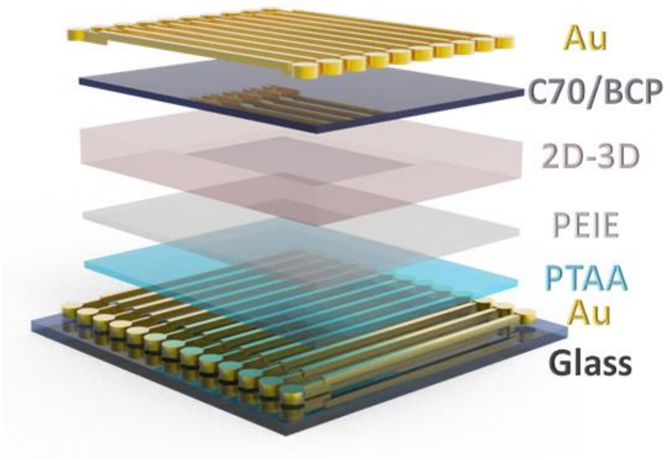
J. Peng, **Q. Lin*** *et al.*, ***Nat. Commun.***, 12: 1531 (2021).

F. Yao, C. Tao*, **Q. Lin***, G. Fang* *et al.*, ***Nat. Commun.***, 11: 1194 (2020).

# Photodetection and Imaging 2



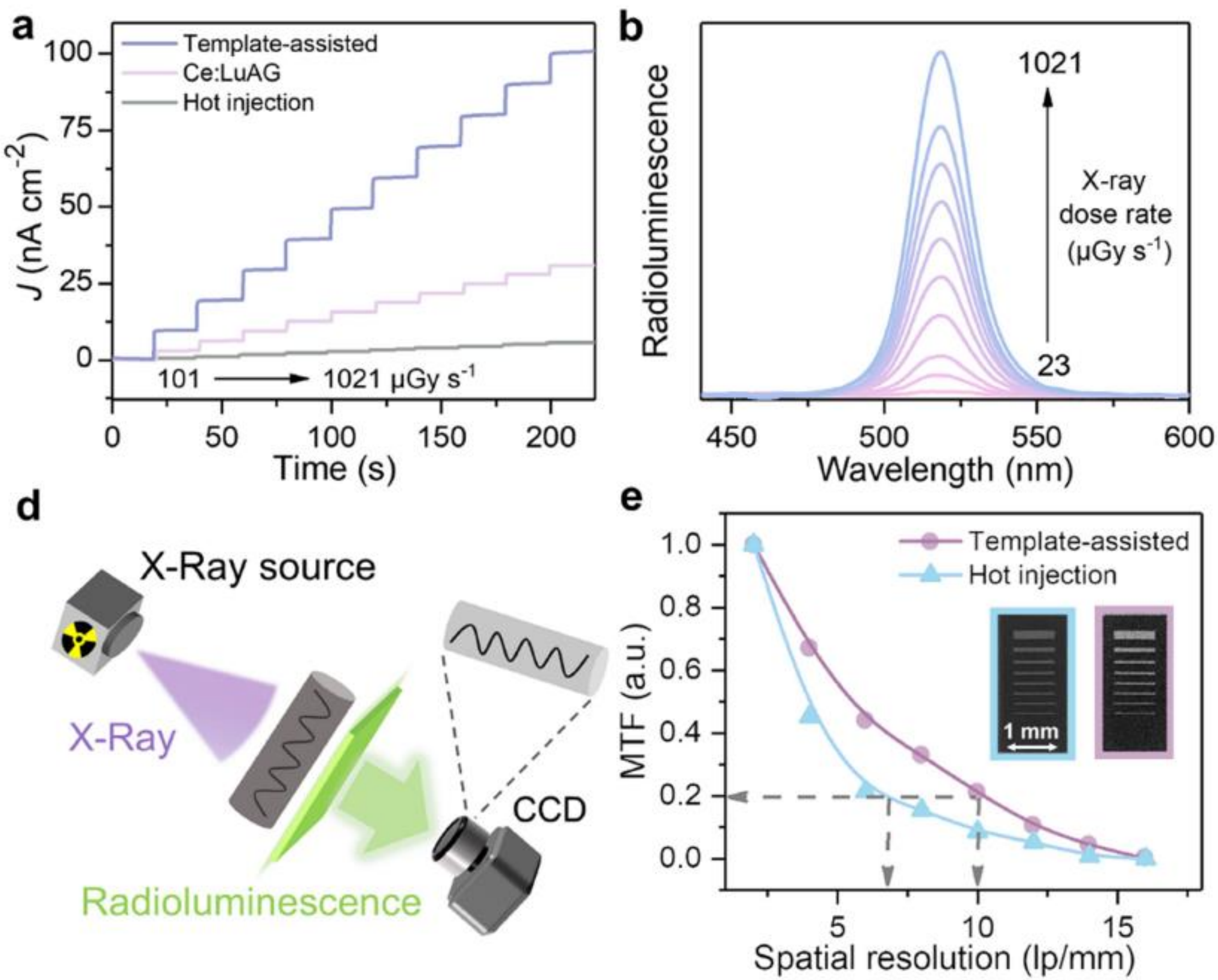

Photodetector array

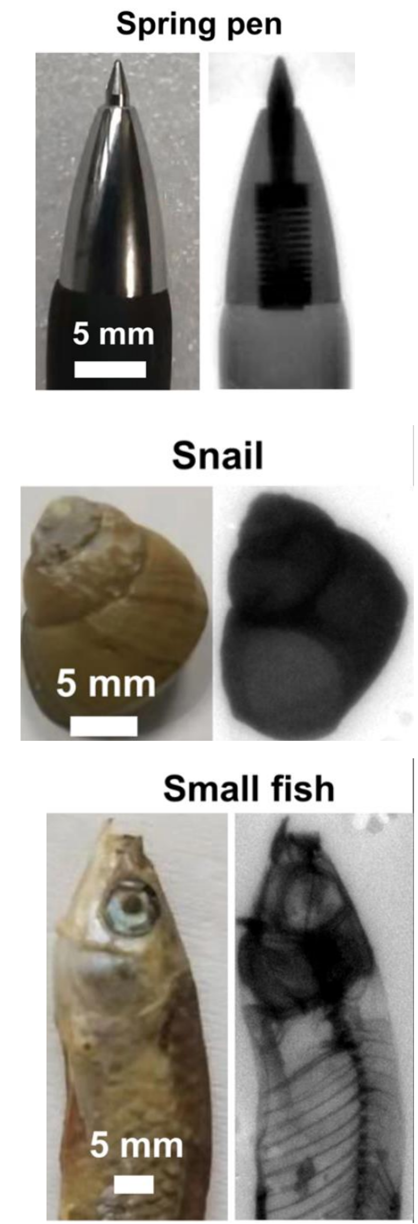



Structure of thin film photodiodes

J. Peng, **Q. Lin*** *et al.*, ***Matter***, 5: 2251-2264 (2022).

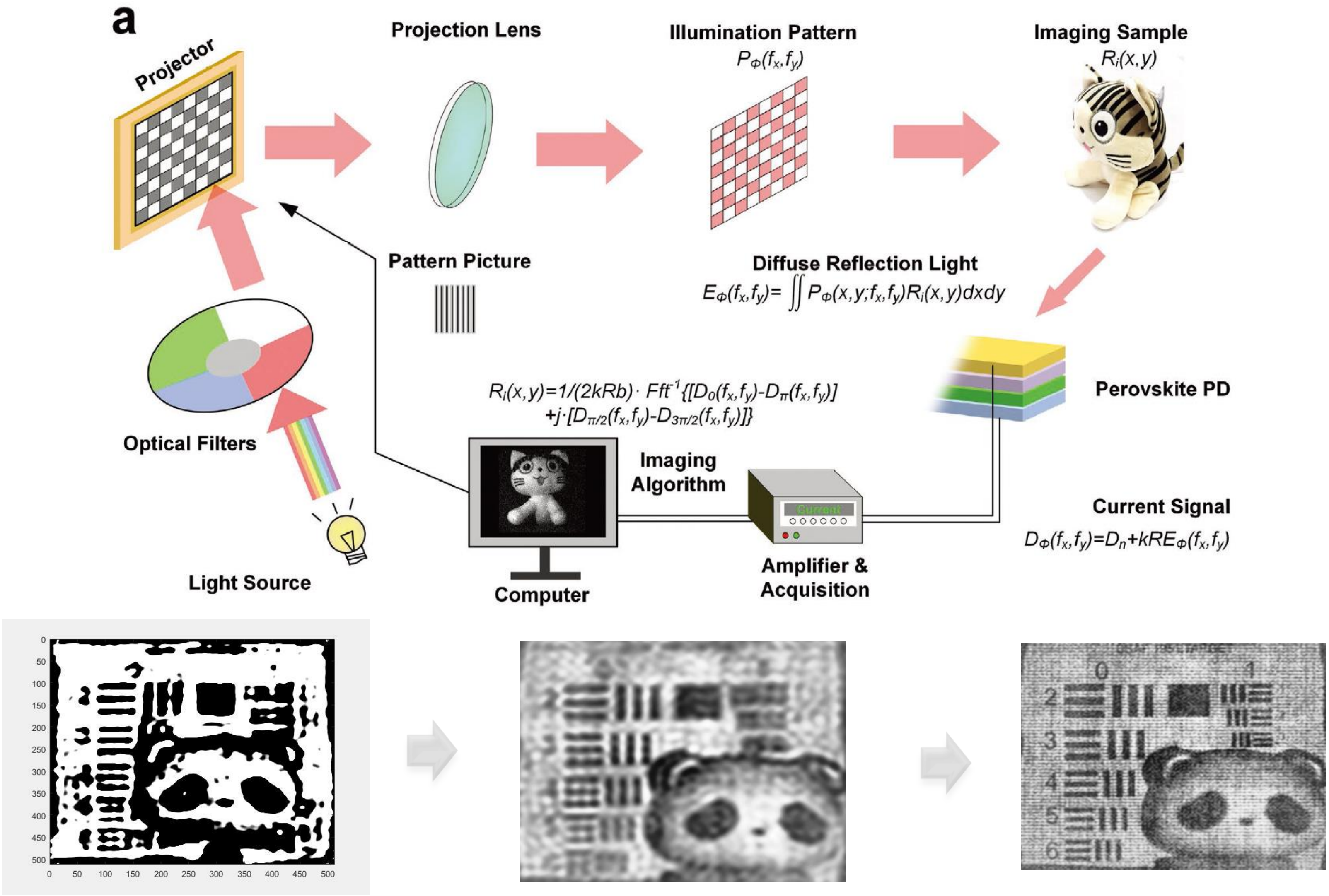
## Photodetection and Imaging 3



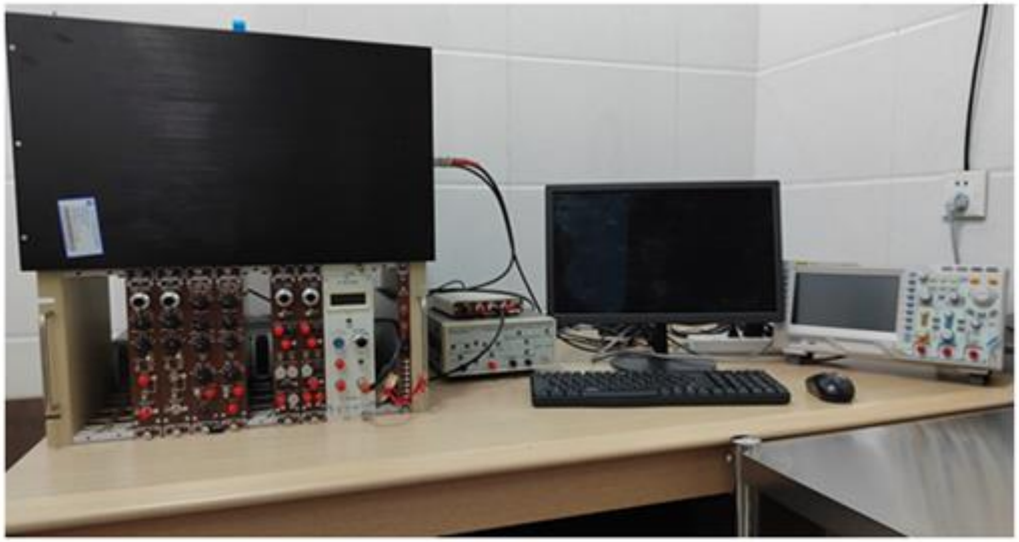

Yu Li, Q. Lin* *et al.*, ***Adv. Opt. Mater.***, 2023, 11: 2023169.

# Photodetection and Imaging 4

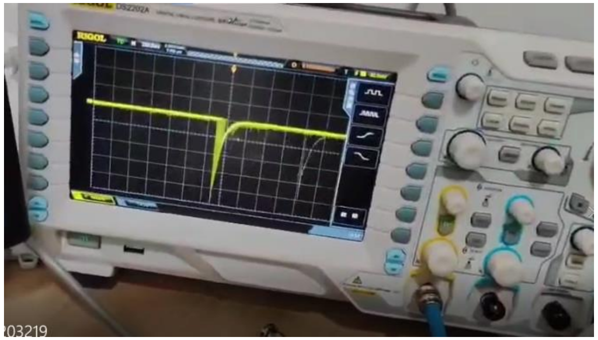


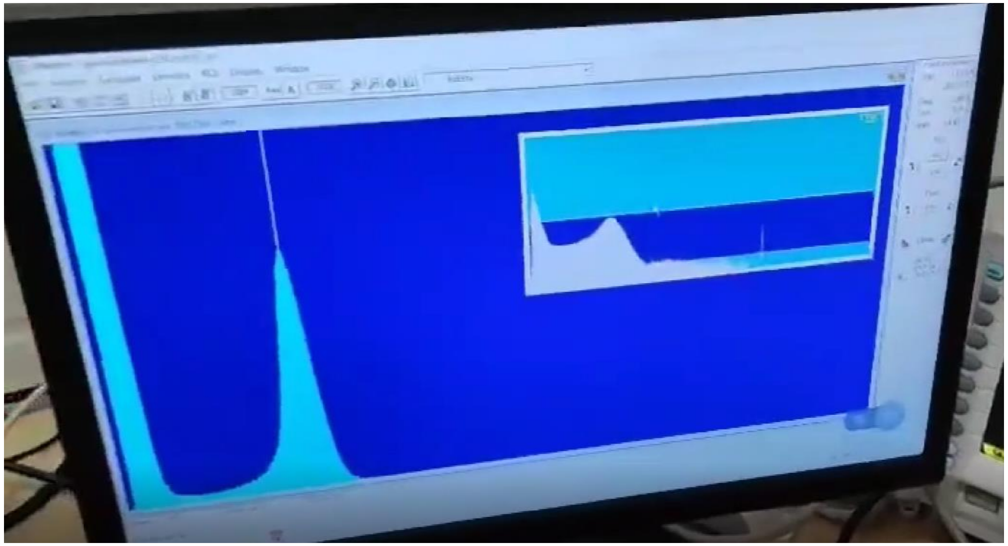

**J. Zhong*, W. Mai*** *et al.*, ***Adv. Funct. Mater.***, 2023, 11: 2023169.

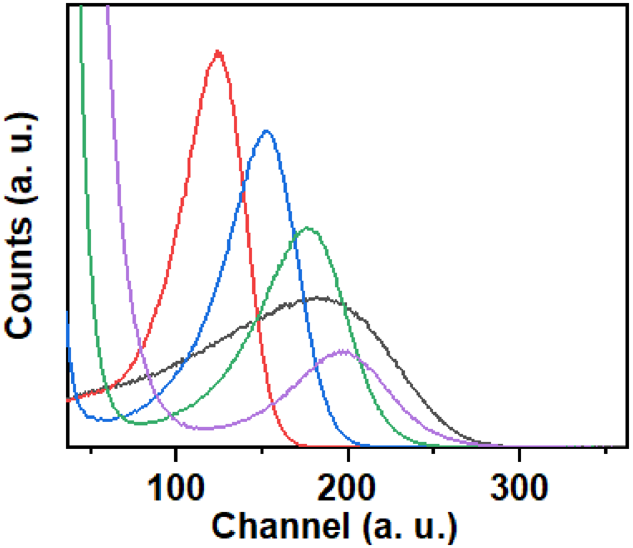
**S. Bai, Q. Lin*** *et al.*, ***under review.***



## Single photon detection of gamma-ray and neutrons

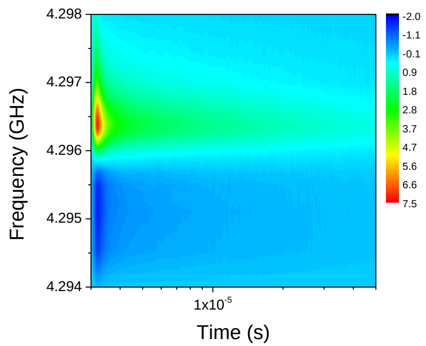


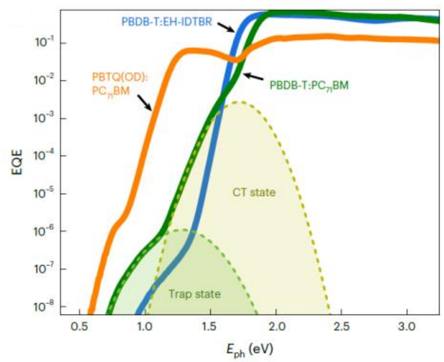


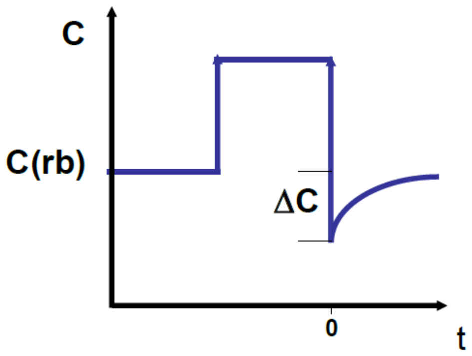


- **Opto-electronic property characterization**:

  TOC, CELIV, SCLC, IPC, DI, TREL, TRPL, TRMC, S-EQE, DLTS;




- **Opto-electronic strategies for device optimization**:

  Optical modeling, temporal response, spectral response.

**Chapter 24**: "**Metal halide perovskites for photodetection**" in the book *Wiley Series in Materials for Electronics and Optoelectronics: Photoconductivity and Photoconductive Materials*.

Group photo 2018

Group photo 2021


Group photo 2022

Group photo 2023

# THANKS