核探测与核电子学国家重点实验室结题汇报

应用于X射线探测的有机无机钙钛矿研究

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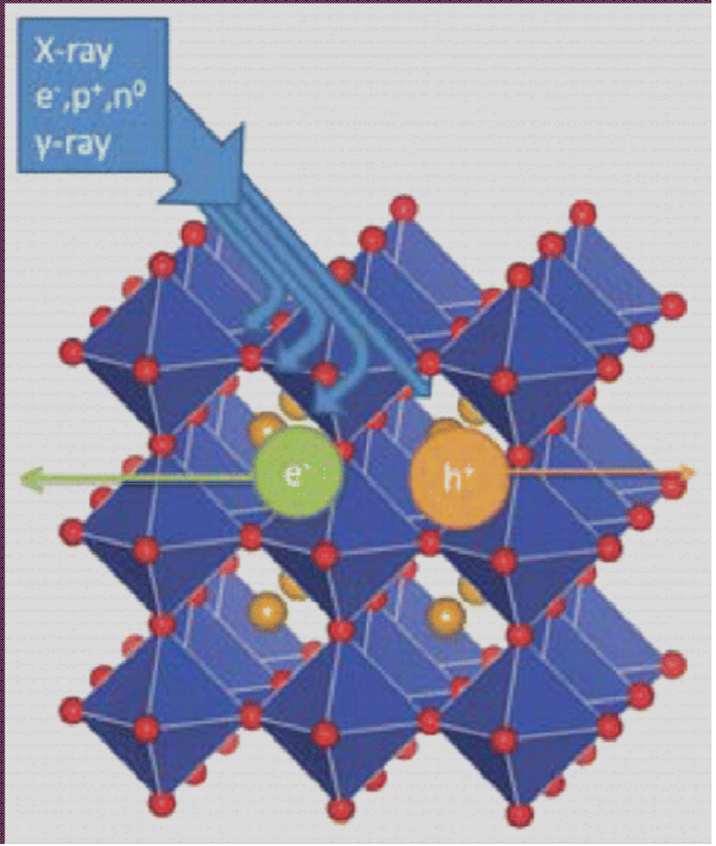
2019年4月23日

报告内容

- 项目背景及研究意义
- 项目研究内容
- 项目研究进展





安全、国防、医学影像、工业材料检验、核电站及科研

两种方法

间接转化法： x射线辐射是通过利用闪烁体材料将高能x射线转换成光来探测的。

Scintillator-based detector arrays have a limited resolution due to a lateral spread of the scintillated light within the converting layer.

direct converters, which are amorphous or polycrystalline semiconductors, are limited in their time response, causing effects such as ghosting. Perfect direct converters would be single crystals, which are expensive and cannot be grown in arbitrary sizes.

直接转化法： x射线辐射通过利用直接转换器将高能x射线直接转换成电信号来检测的。

直接转化法避免了间接转化法备受折磨的串光现象，然而，直接转化法使用的多晶Se材料对高能X-射线吸收较差，限制了其更广阔的应用。不管是CsI还是α-Se材料，都无法实现在人体所需最低剂量条件下实现X-射线成像检测。

目前用于直接法X射线探测的主要材料

Amorphous Se (a-Se), PbI_2 , HgI_2, CdTe , CdZnTe .

基于a-Se的探测器已商用，但由于其在50 keV以上的光谱范围内吸收系数较低，限制了其在乳腺摄影中的应用。

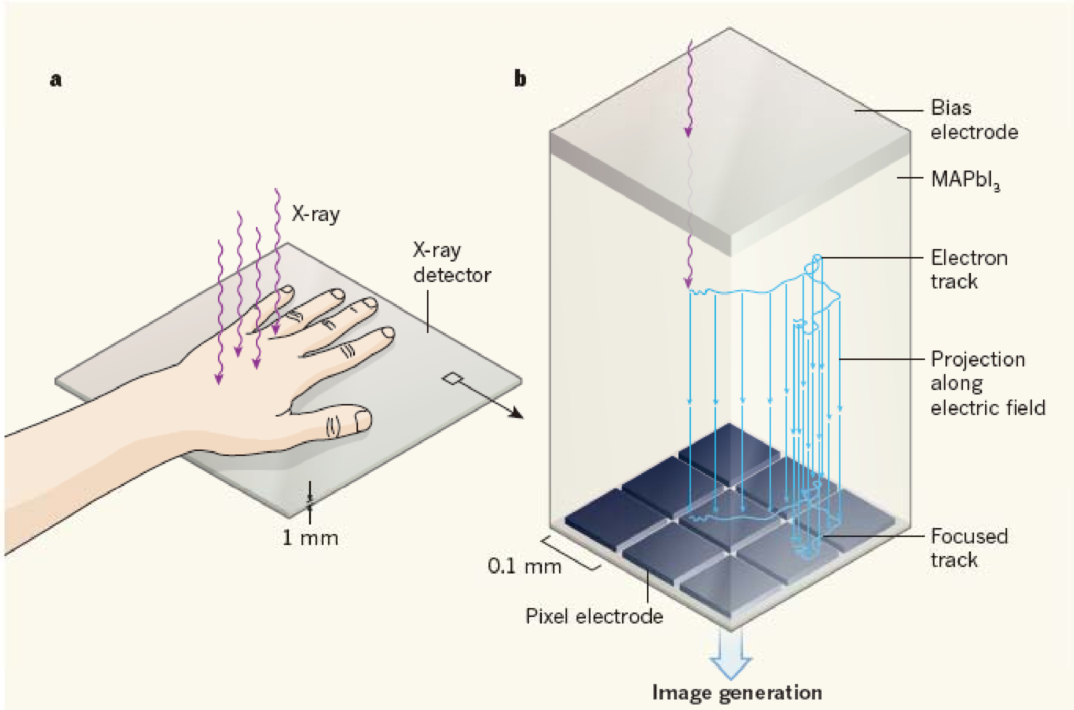
PbI_2 and HgI_2 探测器面临的稳定性问题阻碍了它们的广泛应用

大量的工作正致力于CdZnTe，但规模更大尺寸晶圆和高载流子捕获等问题仍有待克服。

MEDICAL IMAGING

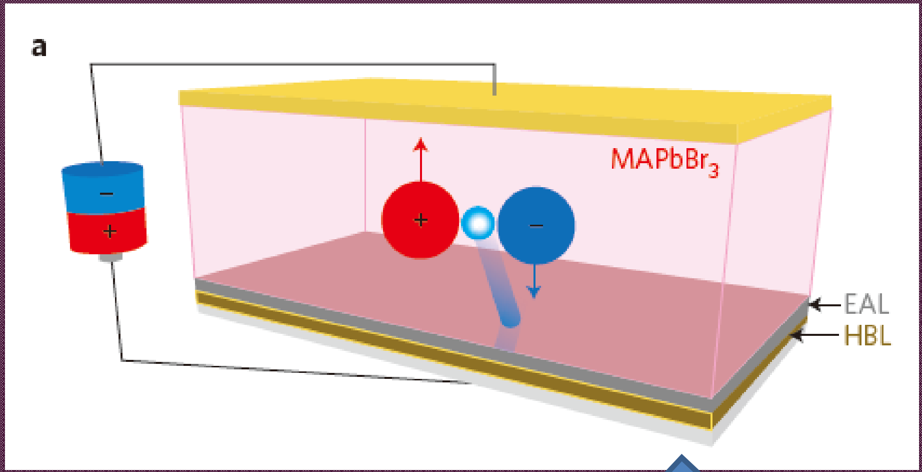
Material change for X-ray detectors

The X-ray sensitivity of radiology instruments is limited by the materials used in their detectors. A material from the perovskite family of semiconductors could allow lower doses of X-rays to be used for medical imaging. **SEE LETTER P.87**



$MAPbI_3$ (Fig. 1). As expected, the material has a high sensitivity to X-rays — almost ten times higher than that of amorphous selenium or CsI. Using the same approach, it should be possible to make detectors that have much larger areas, as required for other medical procedures such as chest X-rays[4]. The sensitivity and processability of this perovskite could therefore reduce the radiation dose needed for medical X-rays to the fundamental quantum and spatial resolution limits.

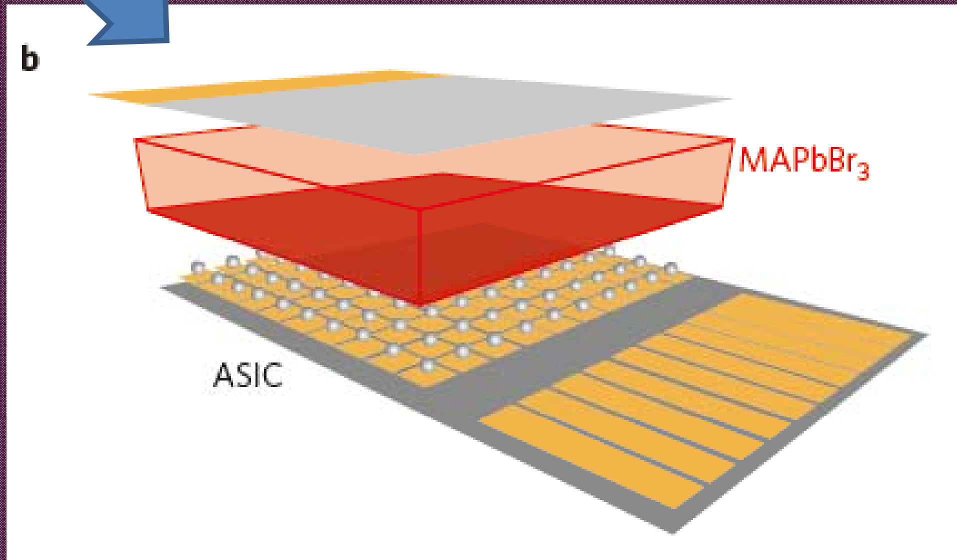
“The potential improvements associated with using $MAPbI_3$ could make a big difference to medical procedures.”



Sketch of the device structure, comprising a $MAPbBr_3$ SC, an electron-accepting layer (EAL), a hole-blocking layer (HBL) and two metallic contacts. Photoexcitation (light blue) excites electrons and holes that contribute to the photocurrent that is driven by an internal field and an external bias.

From single-element detectors towards array imagers.

For X-ray imaging, array detectors could be applied, with an application-specific integrated circuit (ASIC) used for readout, on which the perovskite SC would be bonded via solder bumps.



Current studied perovskite materials used for photodector

$MAPbI_3$, $FAPbI_3$, $MAPbBr_3$, $MAPbBr_{2.94}Cl_{0.06}$, $CsPbI_3$, $Cs_xFA_{1-x}PbI_{3-y}Br_y$

Film(polycrystal), Single –crystal, Wafer

Polycrystalline

Polycrystalline and amorphous converter layers usually suffer from low charge mobility and rely on high applied bias voltages to achieve a sufficiently long schubweg (the average distance a photoexcited carrier drifts before it recombines), which has to match the device thickness.

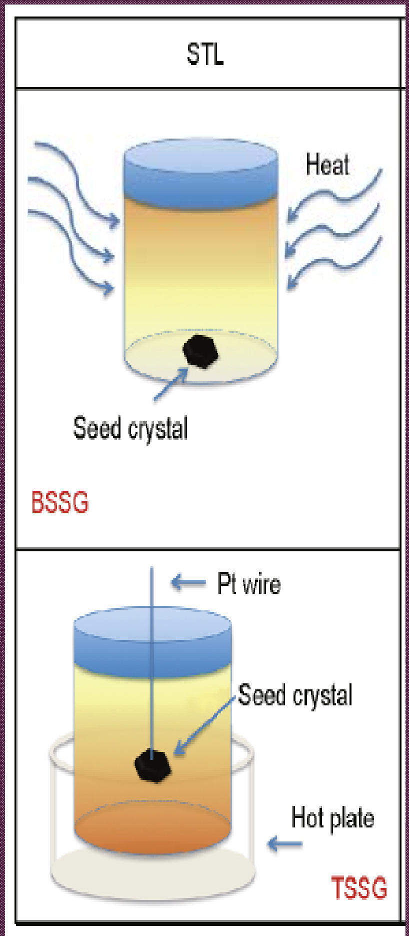
Vs

Single crystalline

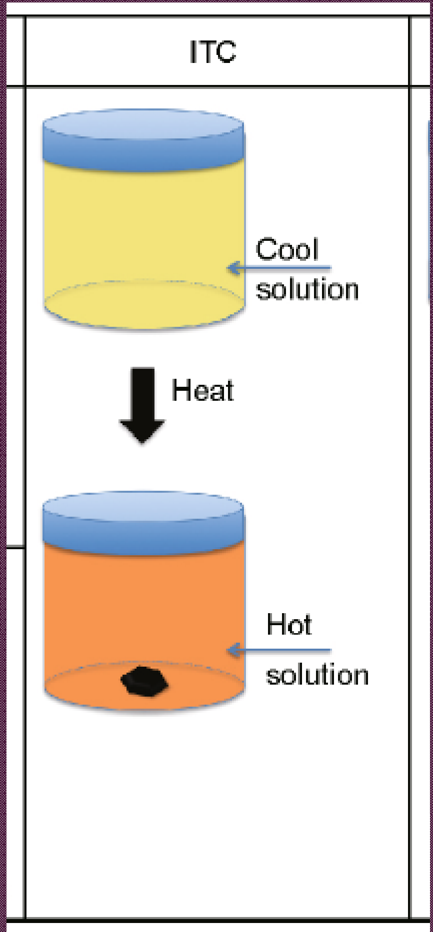
single crystals combine the advantages of high stopping power, low trap density and high charge collection efficiency, which should enable high-sensitivity soft and hard X-ray detection.

单晶生长

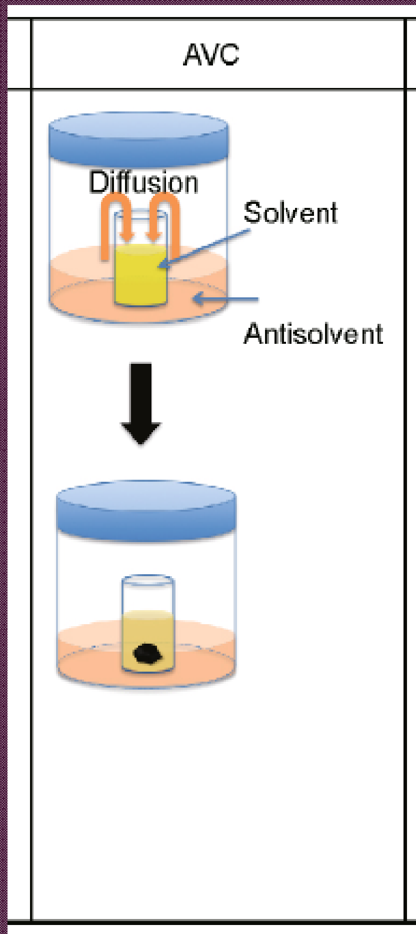
STL：solution temperature-lowering method



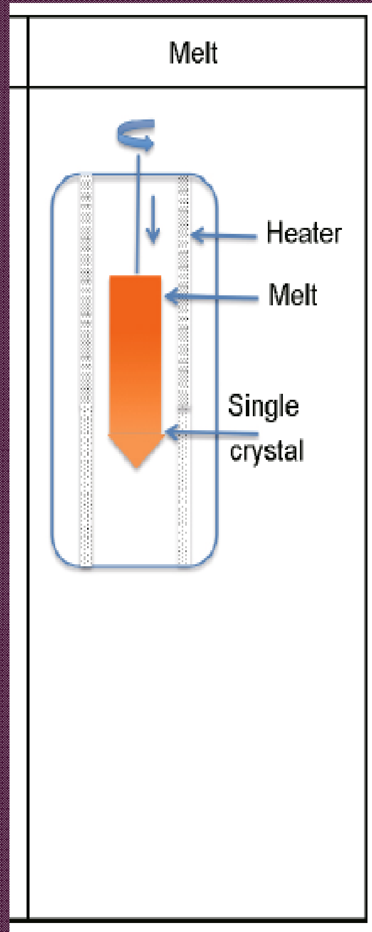
ITC ： inverse temperature crystallization method



AVC: anti-solvent vapor-assisted crystallization method



Melt crystallization



生长$CH_3NH3PbI_3$（$MAPbI_3$）和$MAPbBr_3$

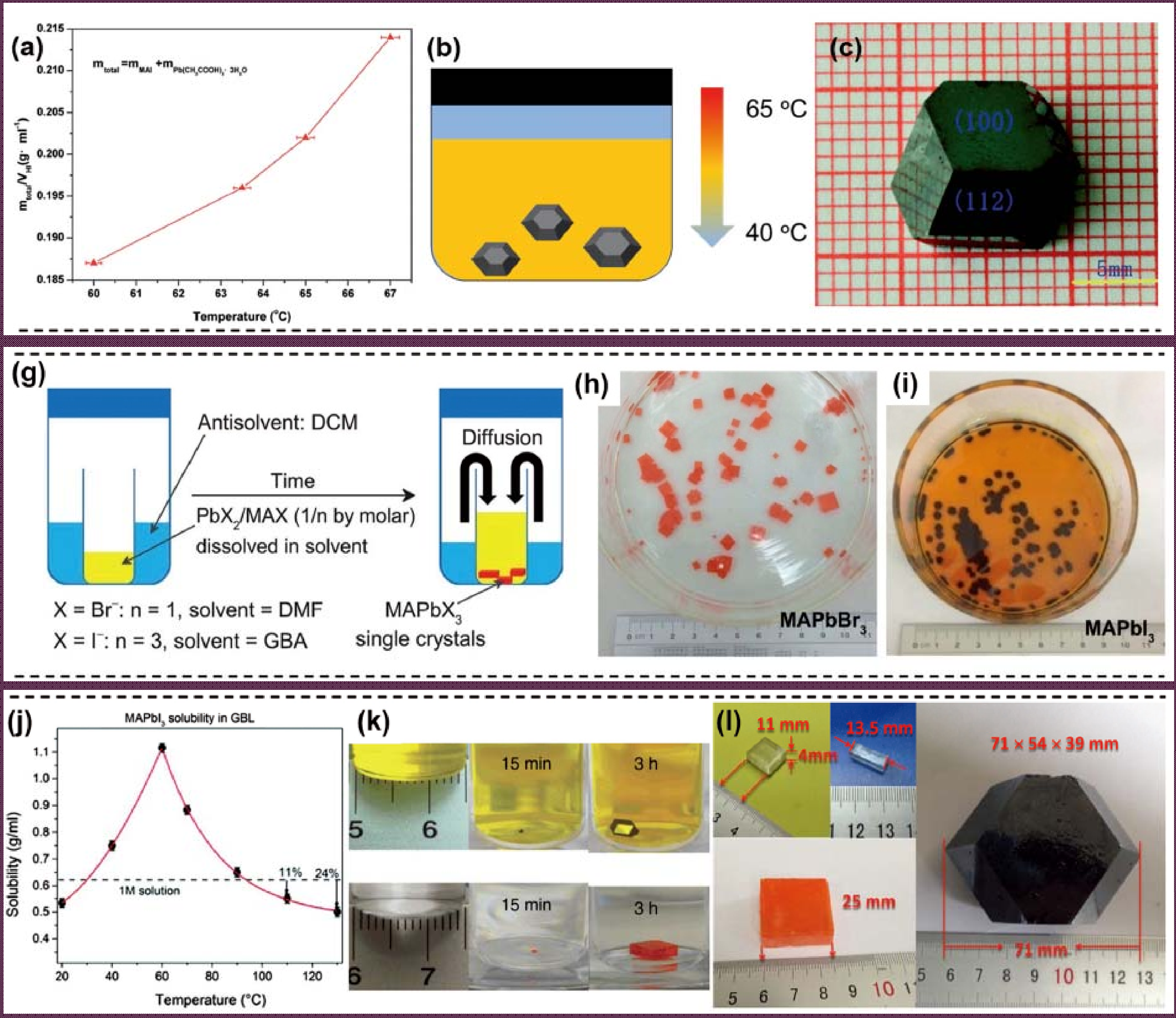
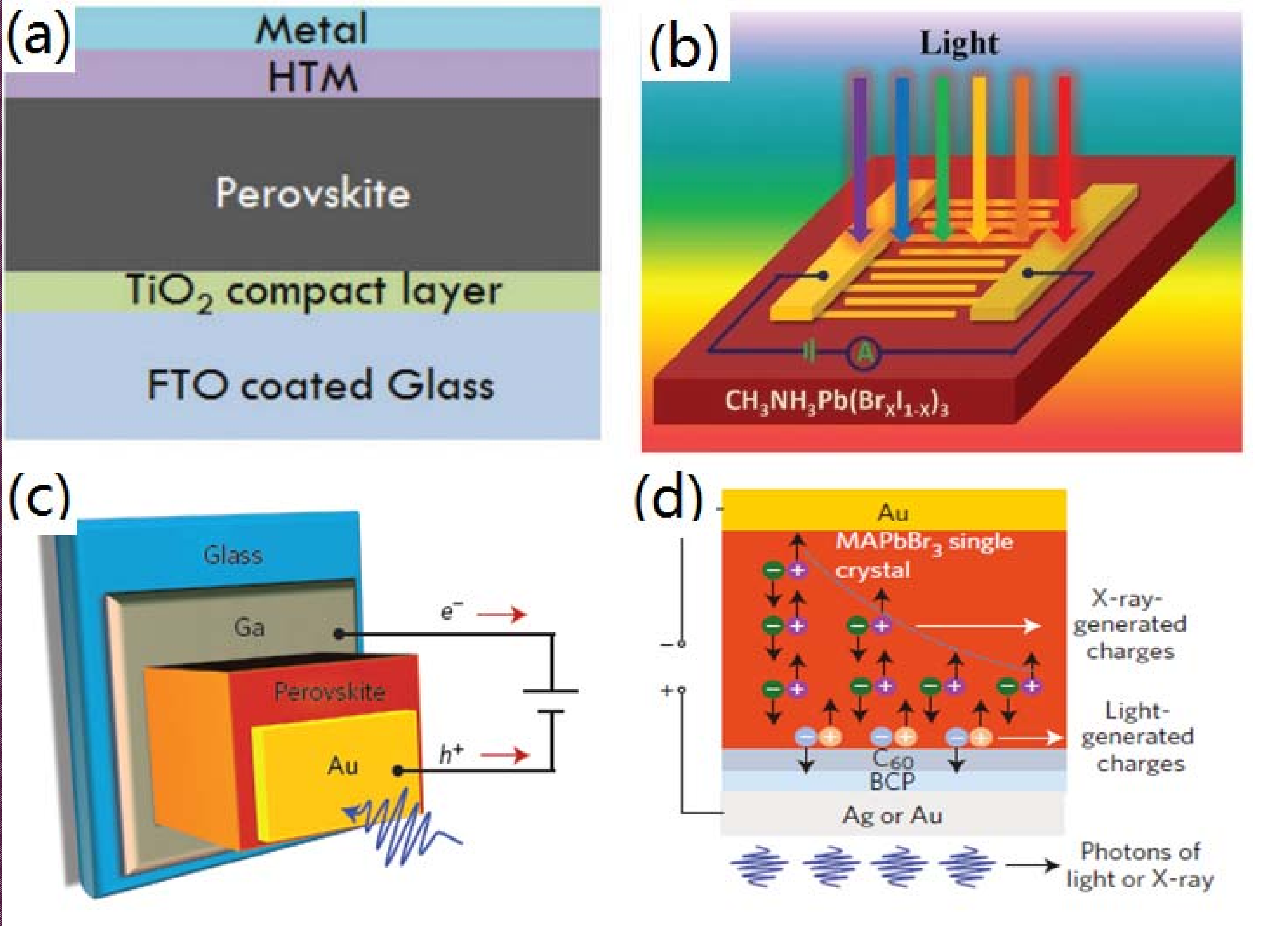


Table 1 A summary of different bulk single crystal growth methods and properties of as grown crystals

Growth method	Single crystal	Properties			Ref.
		Size (mm)	Carrier mobility ($cm^2\ V^{-1}\ s^{-1}$)	Trap state density (cm^{-3})	
STL method	$MAPbI_3$	$10 \times 10 \times 8$			[40]
	$MAPbI_3$	$12 \times 12 \times 7$ (2–4 weeks)	105 ± 35	10^{10}	[42]
	$MAPbI_3$	$10 \times 3.3.$	167 ± 35	7.6×10^8	[35]
	$MAPbI_3$	$20 \times 18 \times 6$ (5 days)			[47]
ITC method	$MAPbI_3$	~5 (3 h)	67.2		[50]
	$MAPbI_3$	$71 \times 54 \times 39$ (3 days to grow 7 mm)	34	1.4×10^{10}	[58]
	$MAPbCl_3$	$11 \times 11 \times 4$	179	1.8×10^9	[58]
	$MAPbBr_3$	$25 \times 25 \times 6$	4.36	2.6×10^{10}	[58]
	$CsPbBr_3$	~8 mm (several hours)	$\sim 2 \times 10^{-4}\ cm^2\ V^{-1}$ (Mobility-lifetime)		[61]
AVC method	$MAPbI_3$	~1	2.5	$\sim 10^9 – 10^{10}$	[34]
Melt crystallization method	$CsPbBr_3$	~7 diameter	1000 $1.7 \times 10^{-3}\ cm^2\ V^{-1}$ (Mobility-lifetime)		[66]

制作探测器

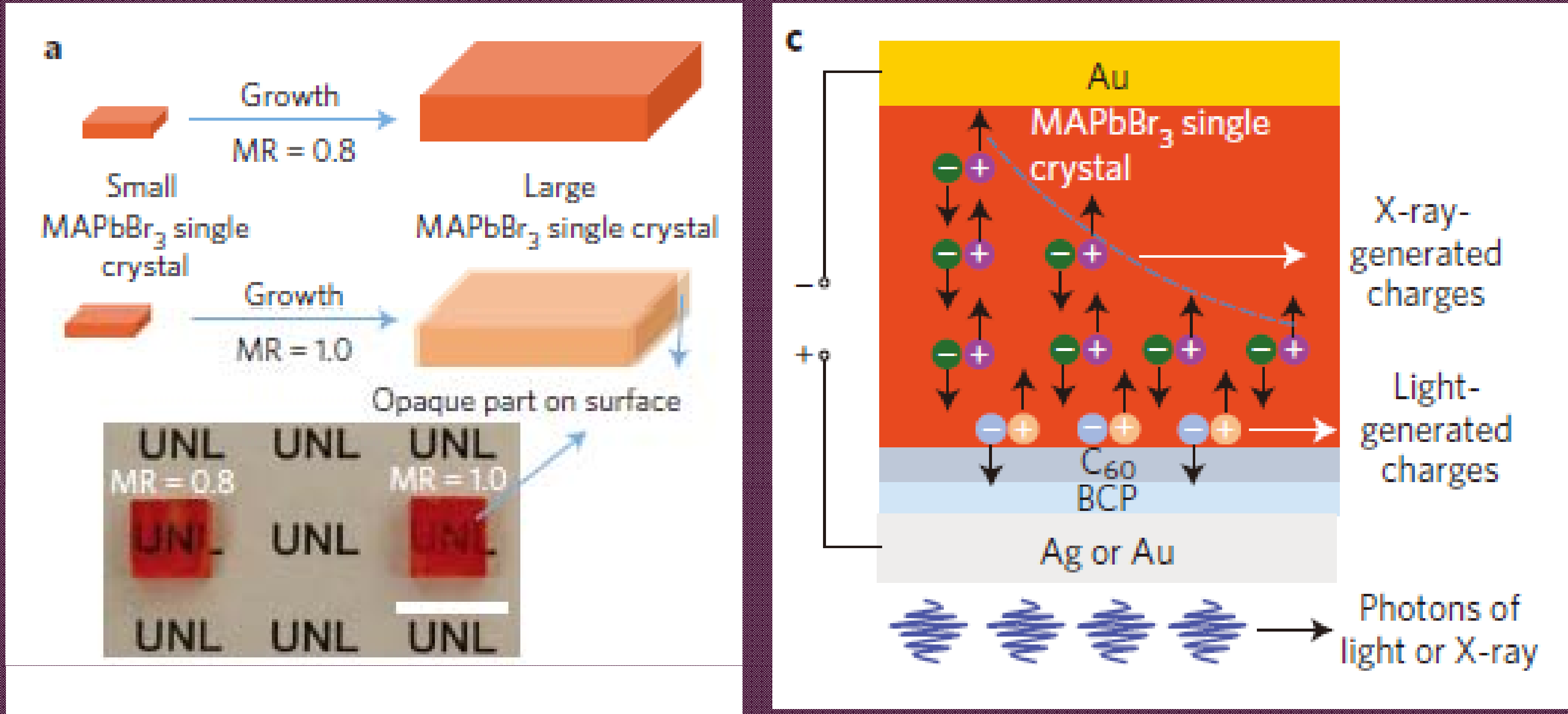
photovoltaic + **photoconductive**



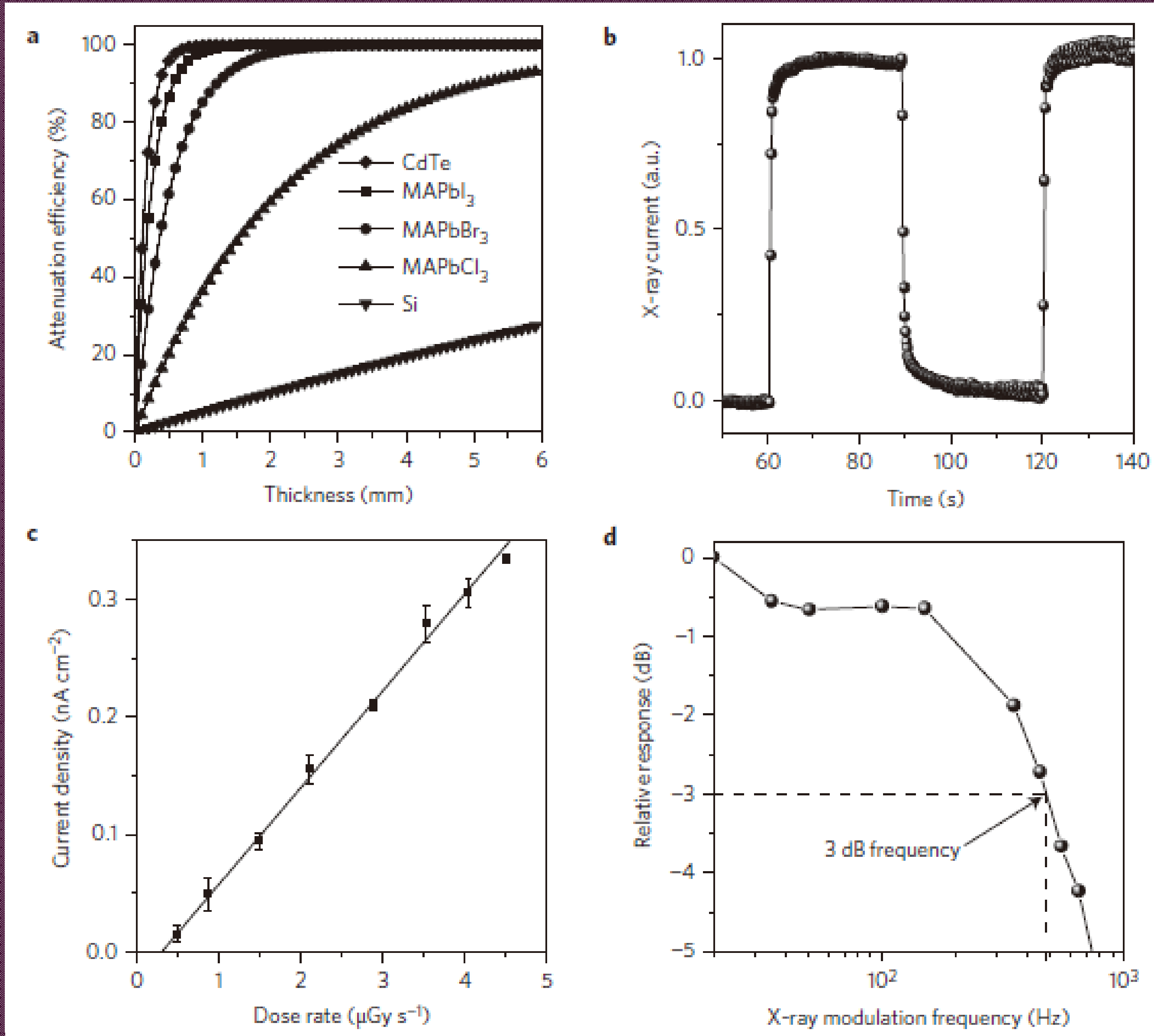
X射线探测

Sensitive X-ray detectors made of methylammonium lead tribromide perovskite single crystals

Haotong Wei[1], Yanjun Fang[1], Padhraic Mulligan[2], William Chuirazzi[2], Hong-Hua Fang[3], Congcong Wang[4], Benjamin R. Ecker[4], Yongli Gao[4,5], Maria Antonietta Loi[3], Lei Cao[2]* and Jinsong Huang[1]*



NATURE PHOTONICS DOI: 10.1038/NPHOTON.2016.41



X-ray detection performance of the MAPbBr3 single-crystal devices.

研究内容及预期目标

单晶生长及表面处理 → 晶体性能测试 → 制作探测器

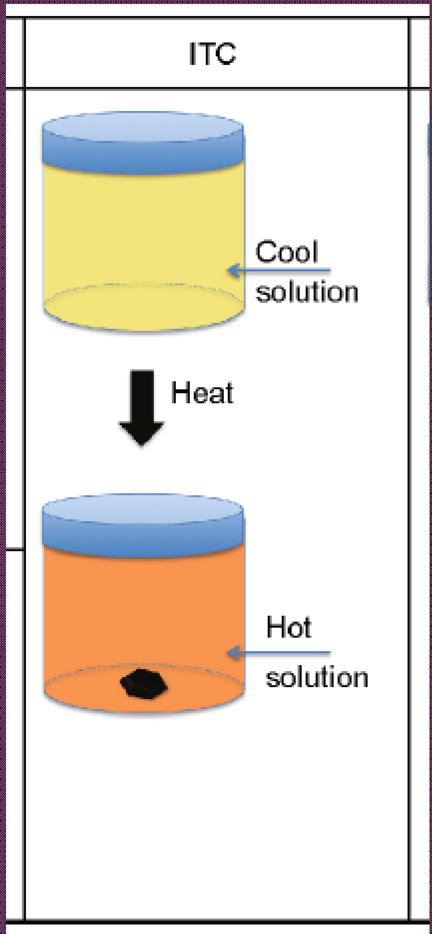
总目标： 掌握单晶生长的最佳工艺条件，制备出高质量的有机无机钙钛矿单晶材料及探 测原型器件，掌握单晶性质对探测器性能的影响机理。

单晶生长及表面处理

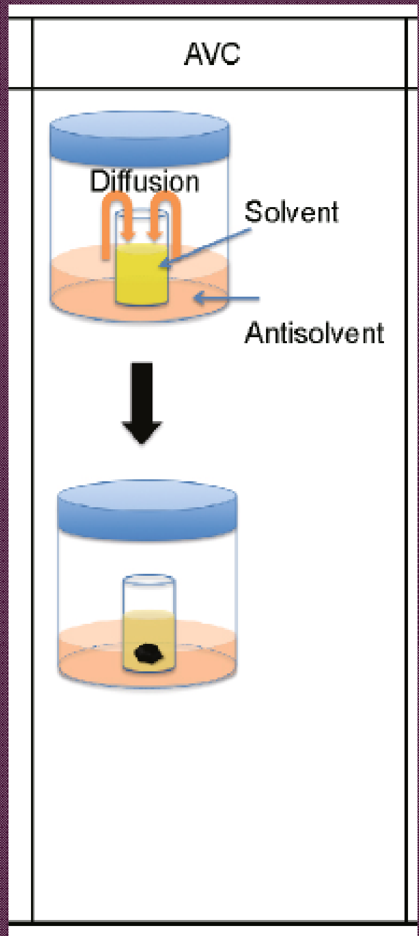
MAPbI$_3$单晶

MAPbBr$_3$单晶

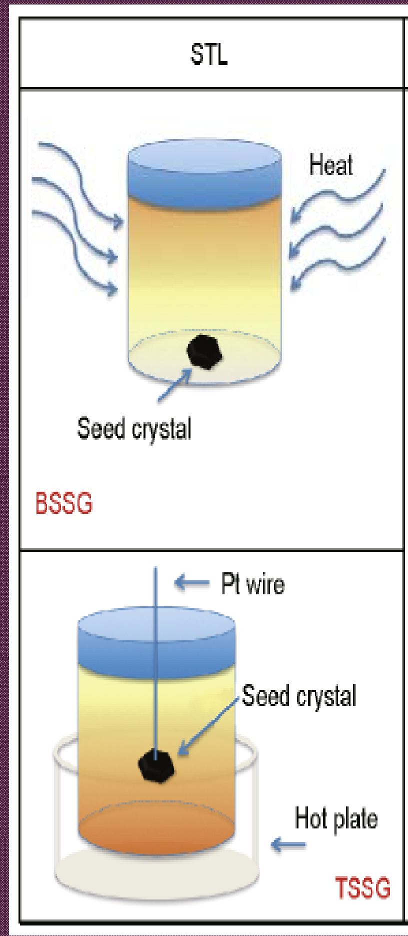
ITC： inverse temperature crystallization method



AVC: anti-solvent vapor-assisted crystallization method



STL：solution temperature-lowering method



生长$MAPbI_3$单晶
(反温度晶化法Inverse temperature crystallization)

1.23M PbI_2
1.23M MAI
GBL (60℃)

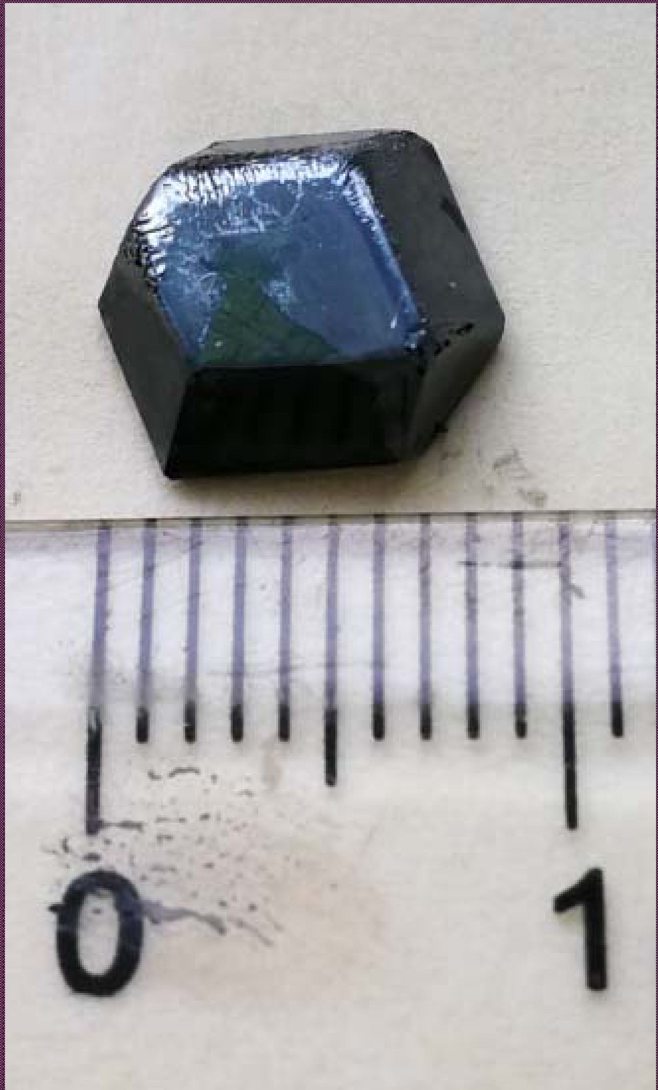
100℃ 20h
0.2um filter

Seed crystal (2mm)

1.23M PbI_2
1.23M MAI
GBL (60℃)

100℃ 1Day

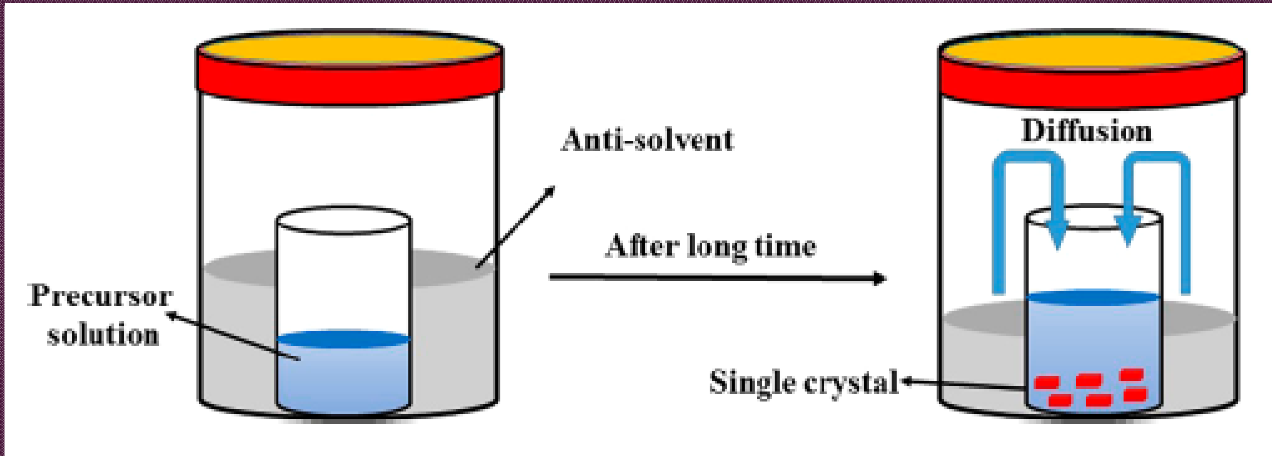
$MAPbI_3$



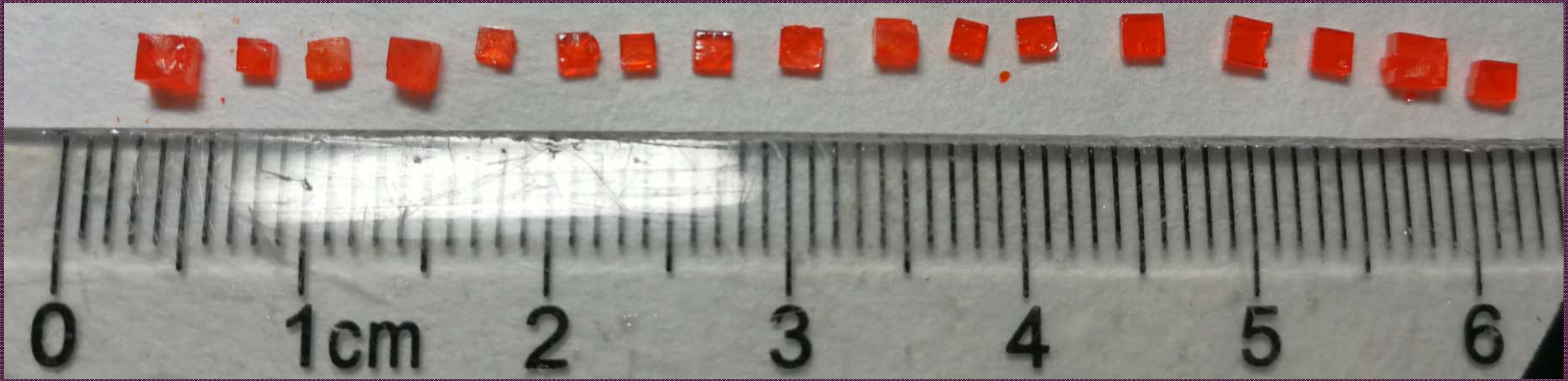
生长两次

生长三次

生长$MAPbBr_3$单晶
(反溶剂气相辅助法Anti-solvent vapor assisted method)

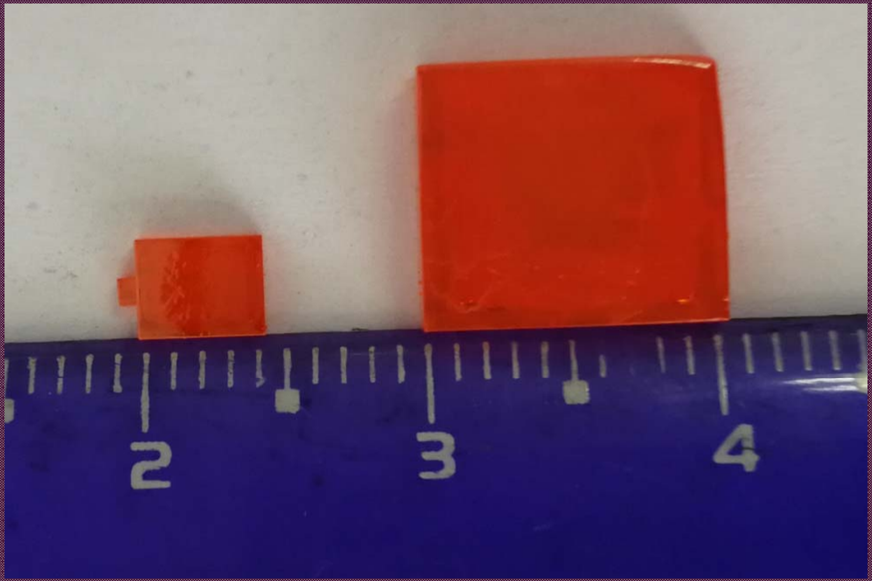


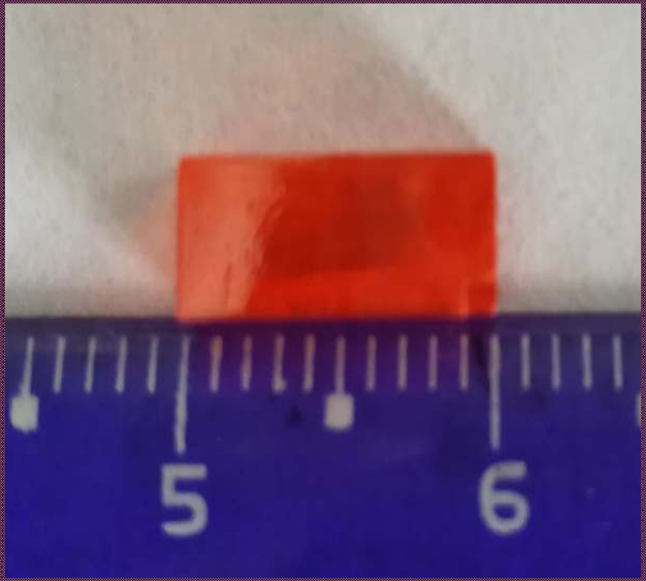
Schematic illustration of antisolvent method for single crystal growth



生长$MAPbBr_3$单晶

低温温度梯度法(low-temperature-gradient crystallization)

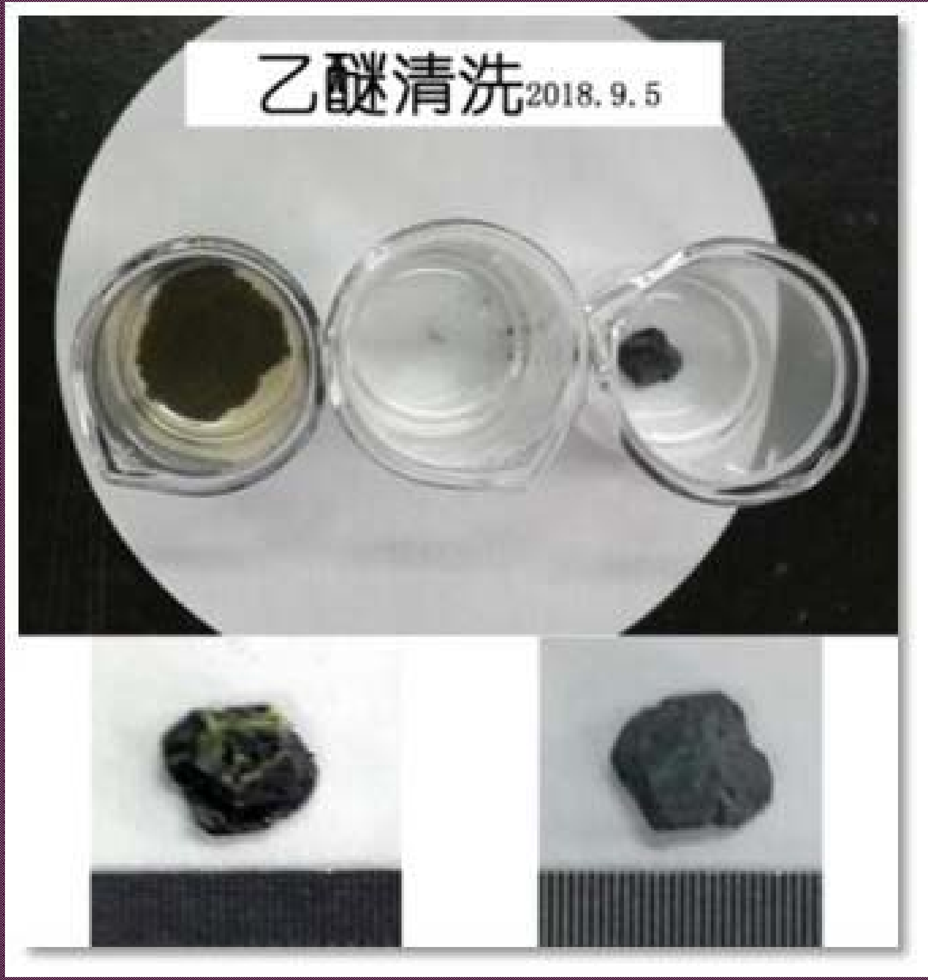




晶体表面处理

目的：降低表面态缺陷，降低漏电流，提高晶体的辐射探测性能。

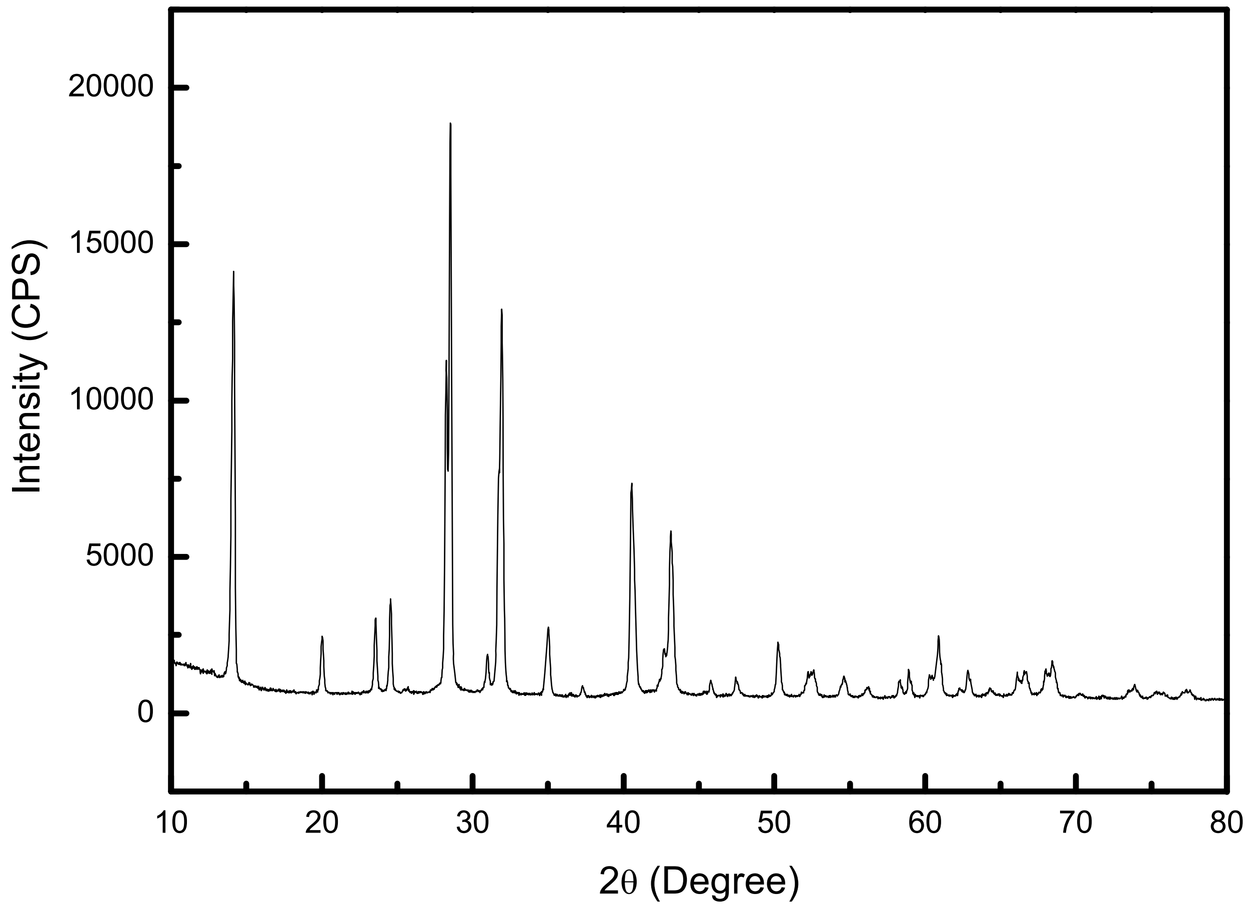
- Ar等离子体
- 化学清洗：将生长好的单晶从生长溶液中取出后用无水乙醚清洗，放入真空干燥箱60℃干燥。



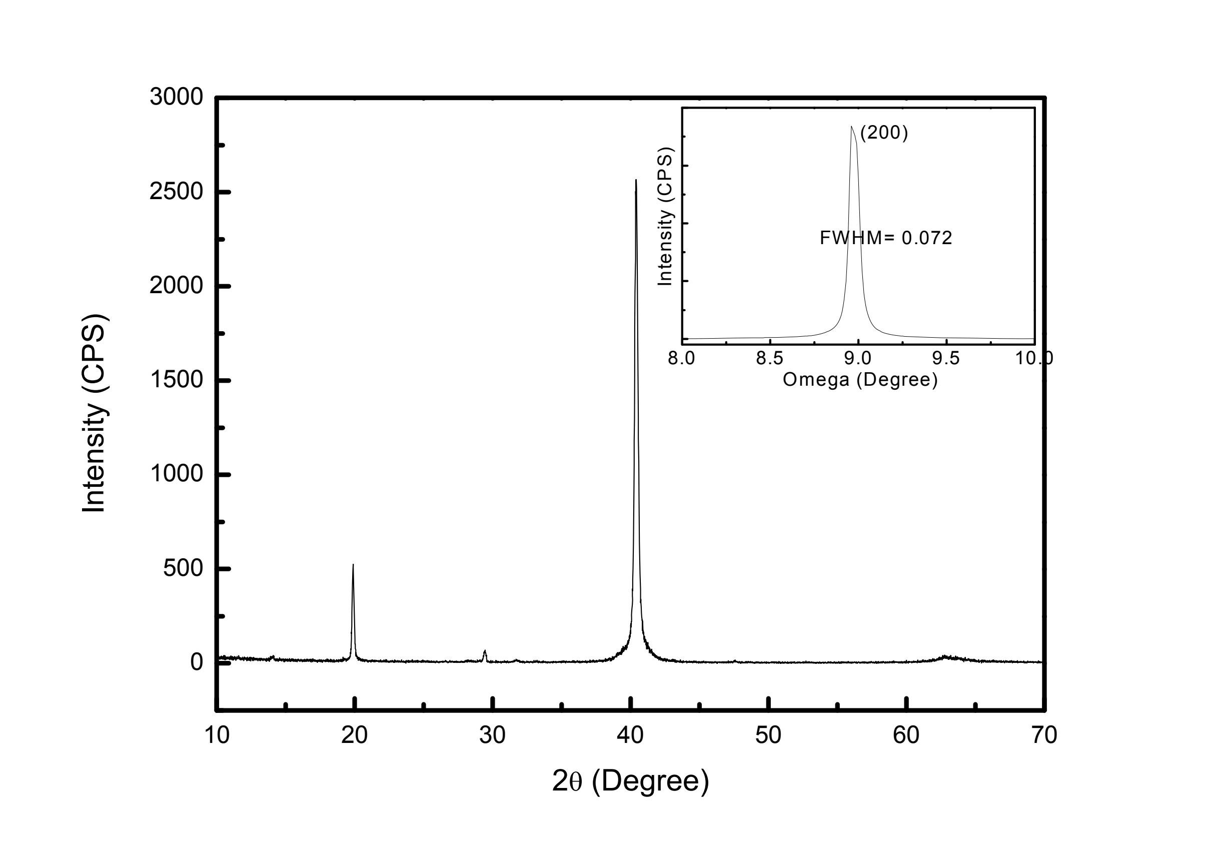
晶体性能测试

- XRD （粉末，单晶，摇摆曲线）
- 空气中的稳定性及热重
- **紫外-可见-红外吸收谱，**发光谱
- 暗态电流-电压曲线、SCLC（迁移率）

$MAPbI_3$ 单晶粉末 XRD

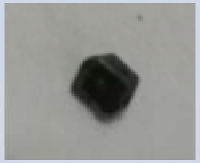


$MAPbI_3$ 单晶 XRD

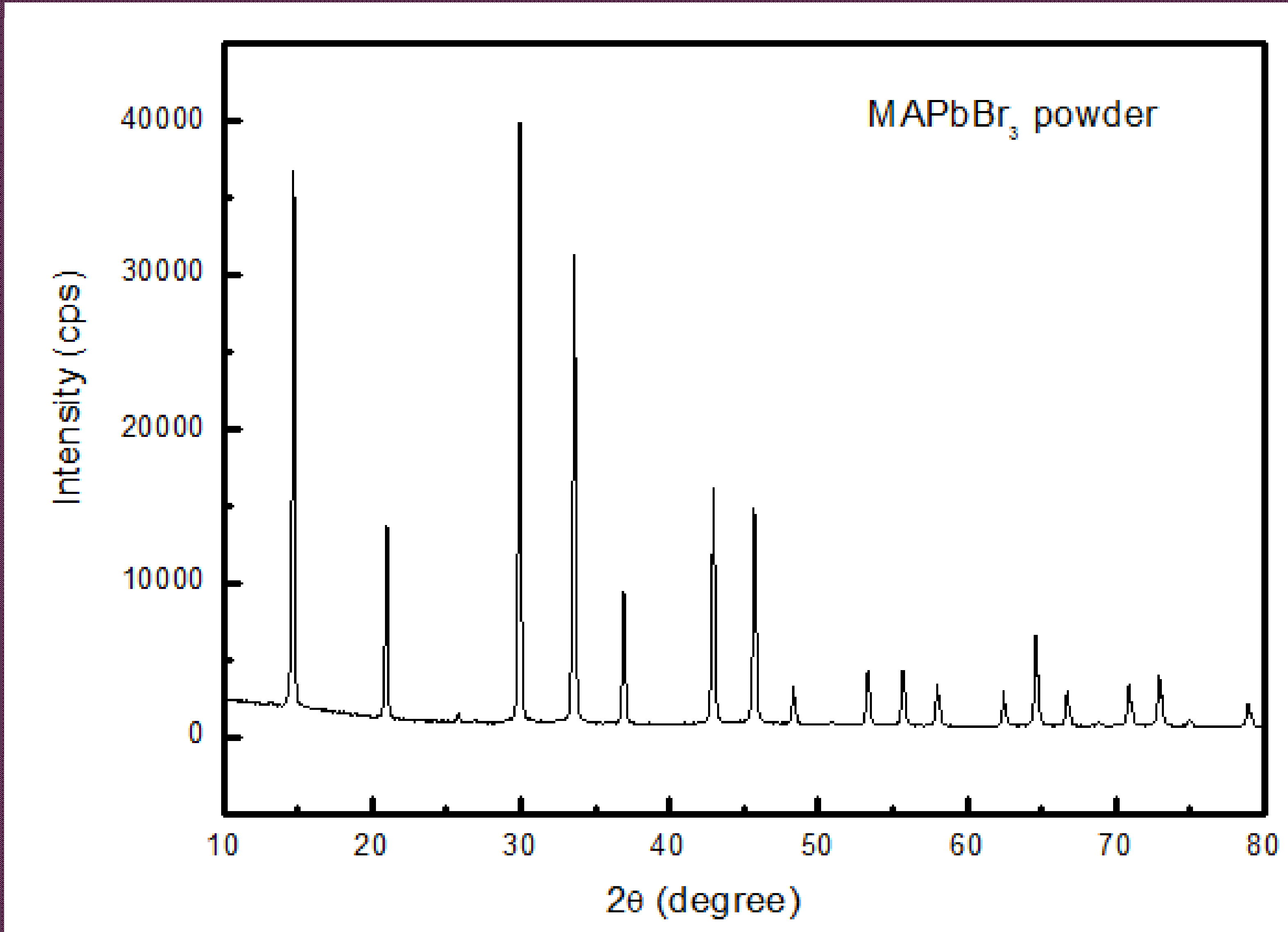


The rocking-curve measurement shows a strong peak at 10.2°, corresponding to the (200) diffraction peak in the 2θ scan mode. The FWHM of the peak is measured 0.072°, indicating that it is a single crystal with respectable crystalline quality.

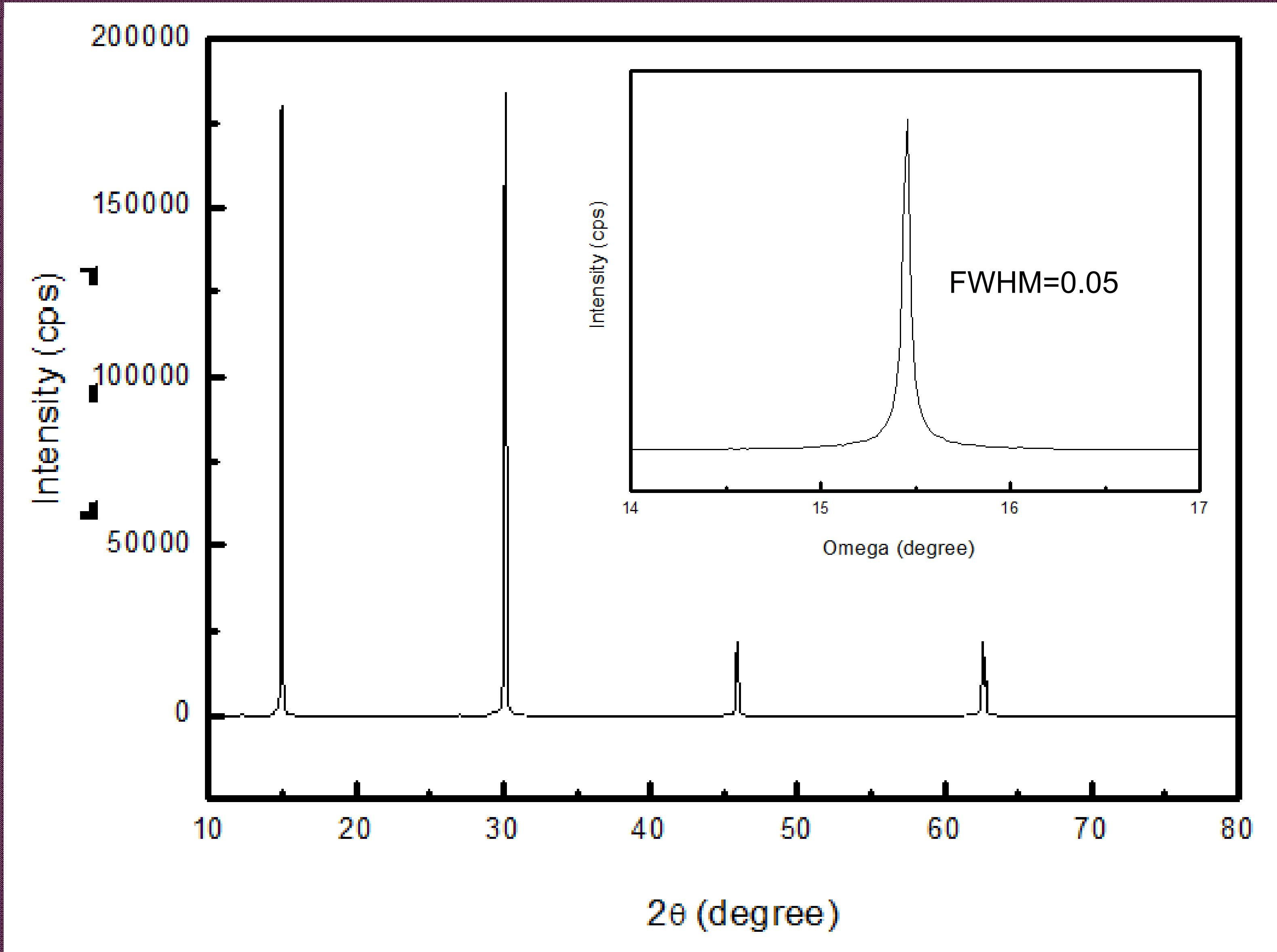
空气中的稳定性

	11.29	12.5	12.12	12.19	12.26	1.10
Box						
air						

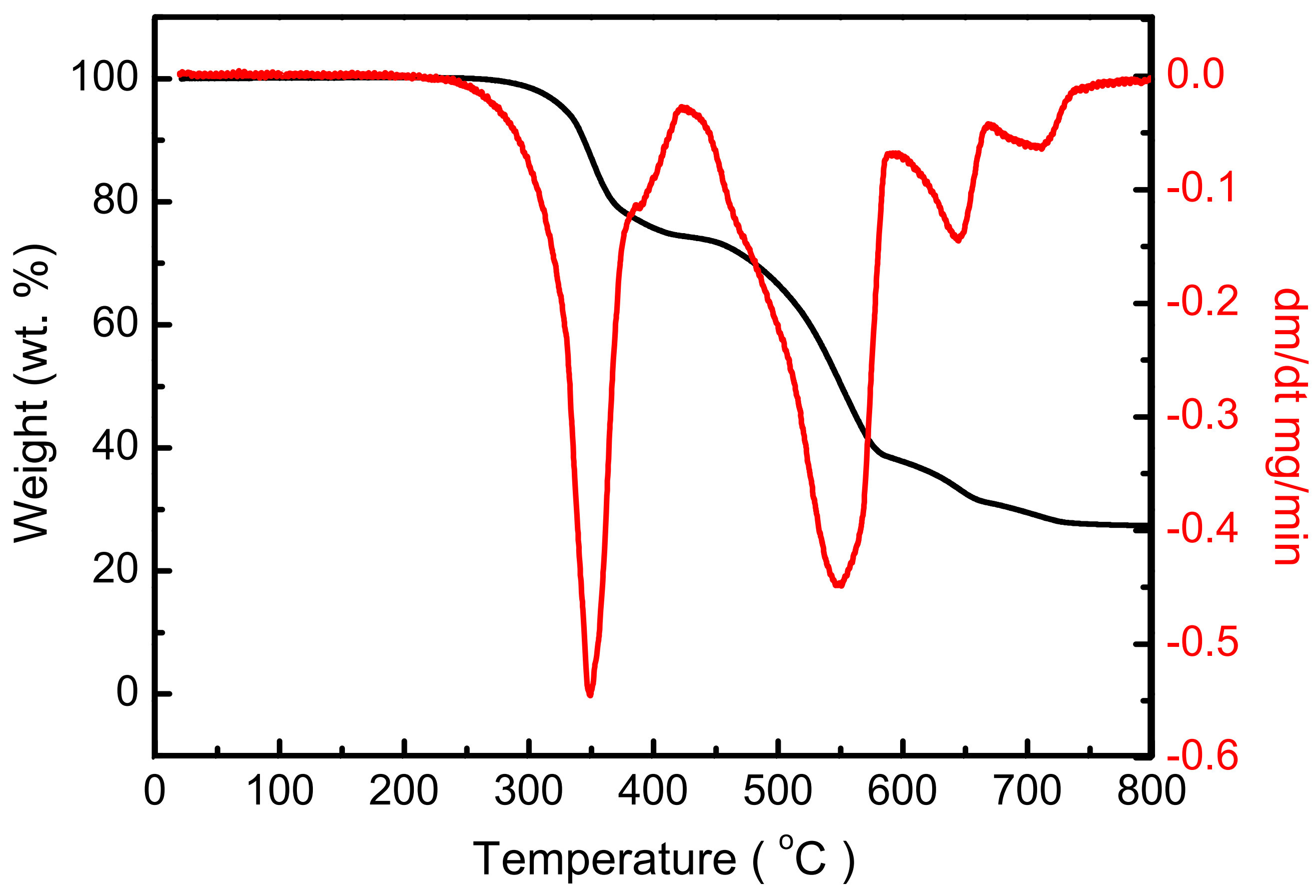
$MAPbBr_3$ 单晶粉末 XRD



MAPbI$_3$ 单晶 XRD

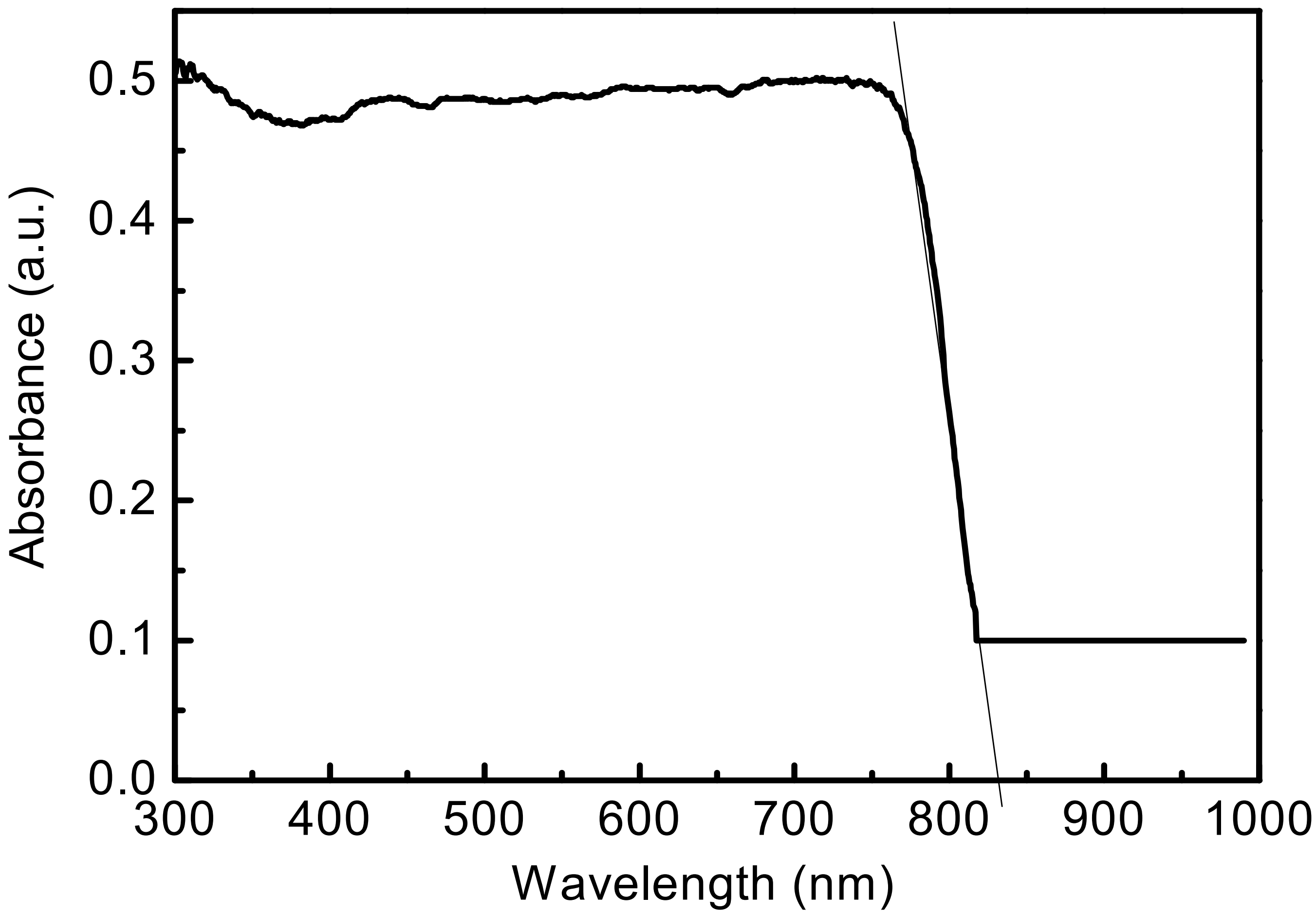


热重曲线



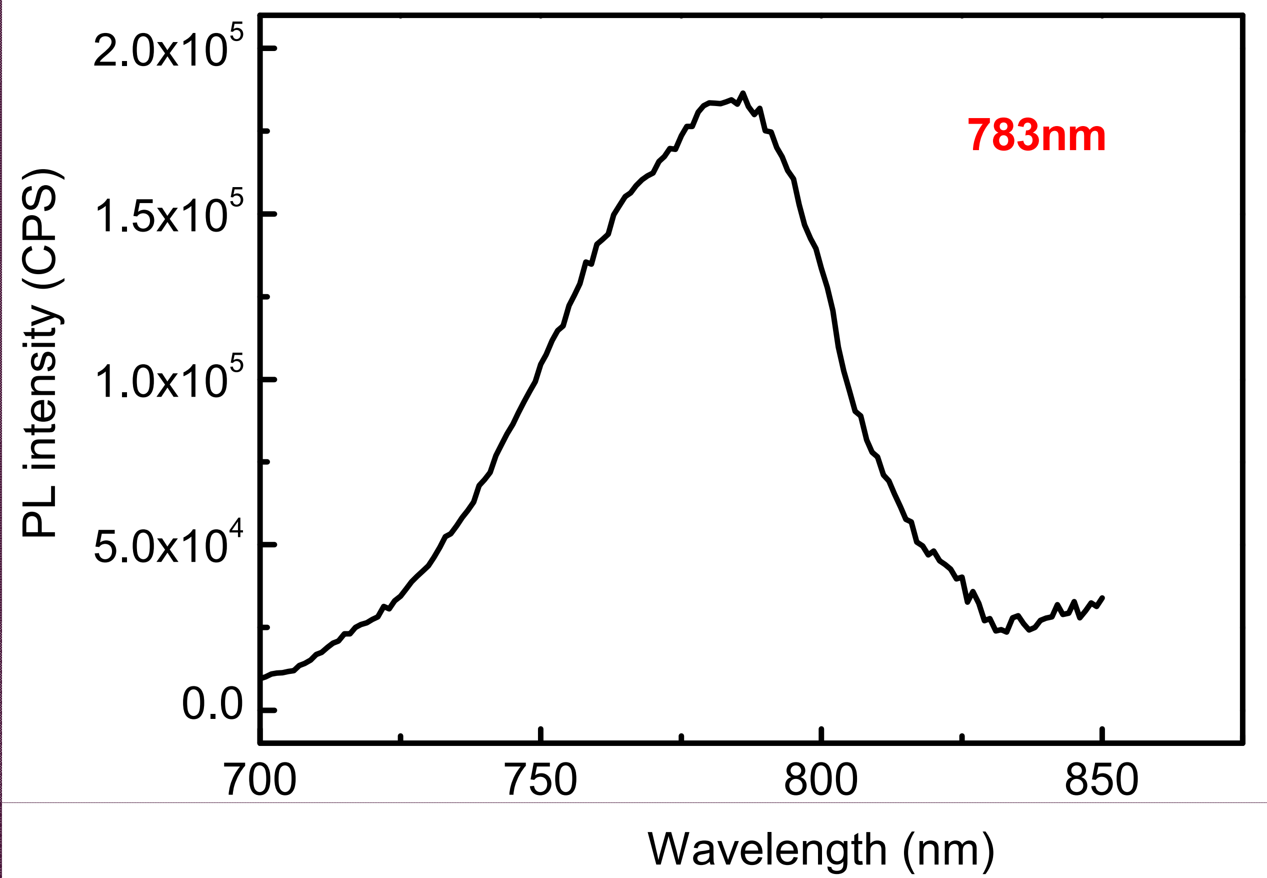
no signature of thermal decomposition is observed until 240 ° C.

紫外-可见-红外吸收谱

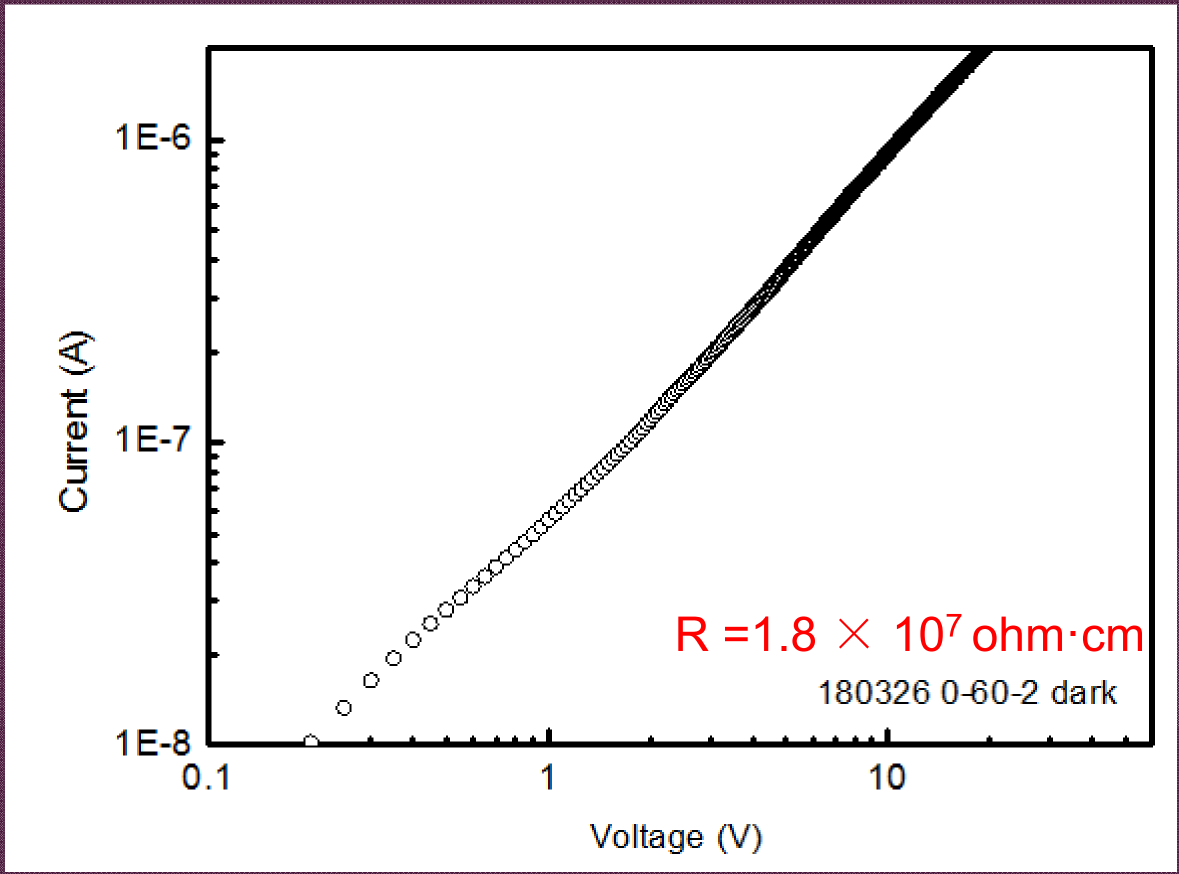


Absorbance (a.u.)
0.0
0.1
0.2
0.3
0.4
0.5
300
400
500
600
700
800
900
1000
Wavelength (nm)

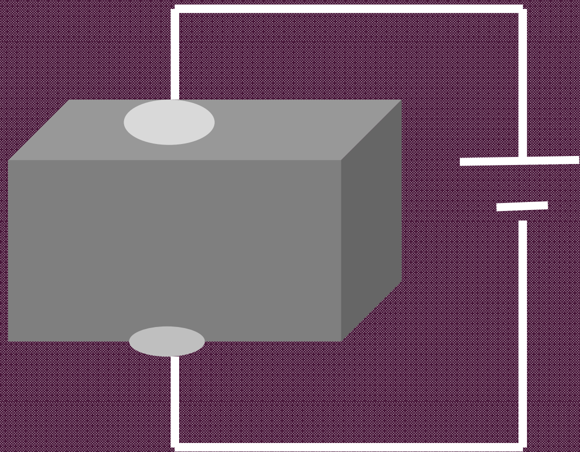
光致发光谱（激光波长532nm）



暗态电流-电压曲线

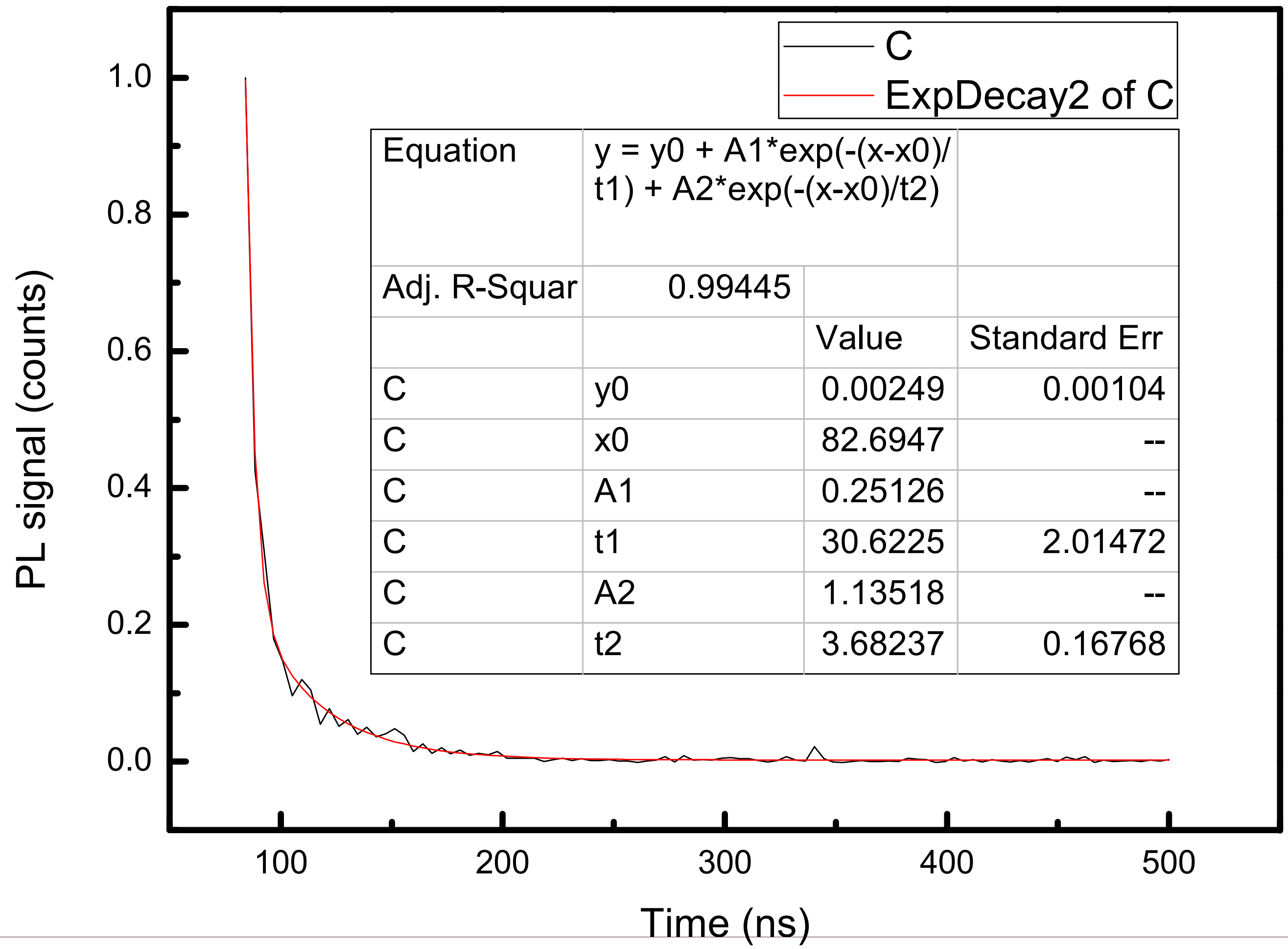


1E-6
1E-7
1E-8
Current (A)
0.1
1
10
Voltage (V)
R =1.8 × 10^7 ohm·cm
180326 0-60-2 dark



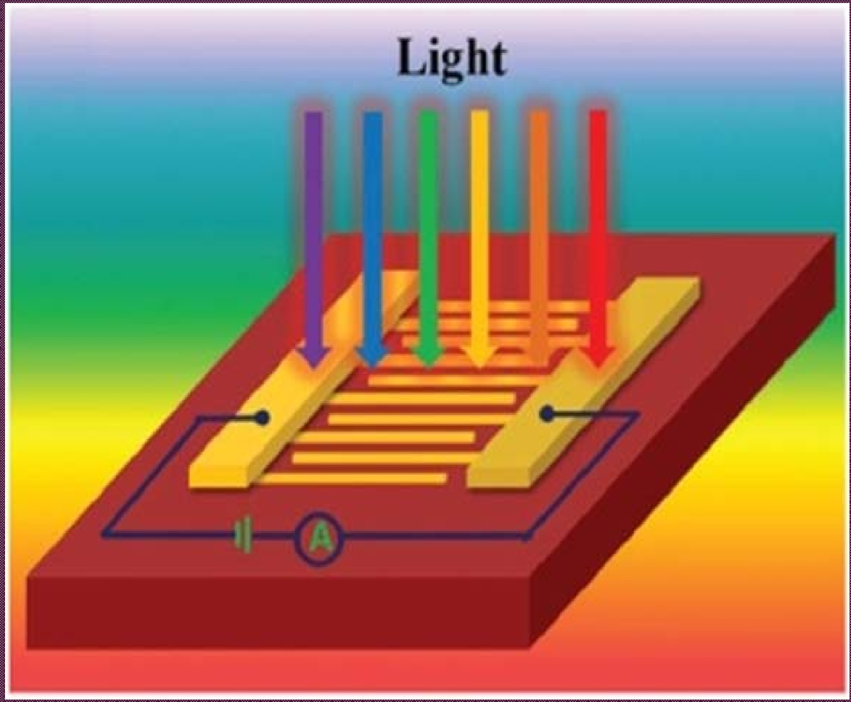
单晶瞬态发光谱（TRPL）

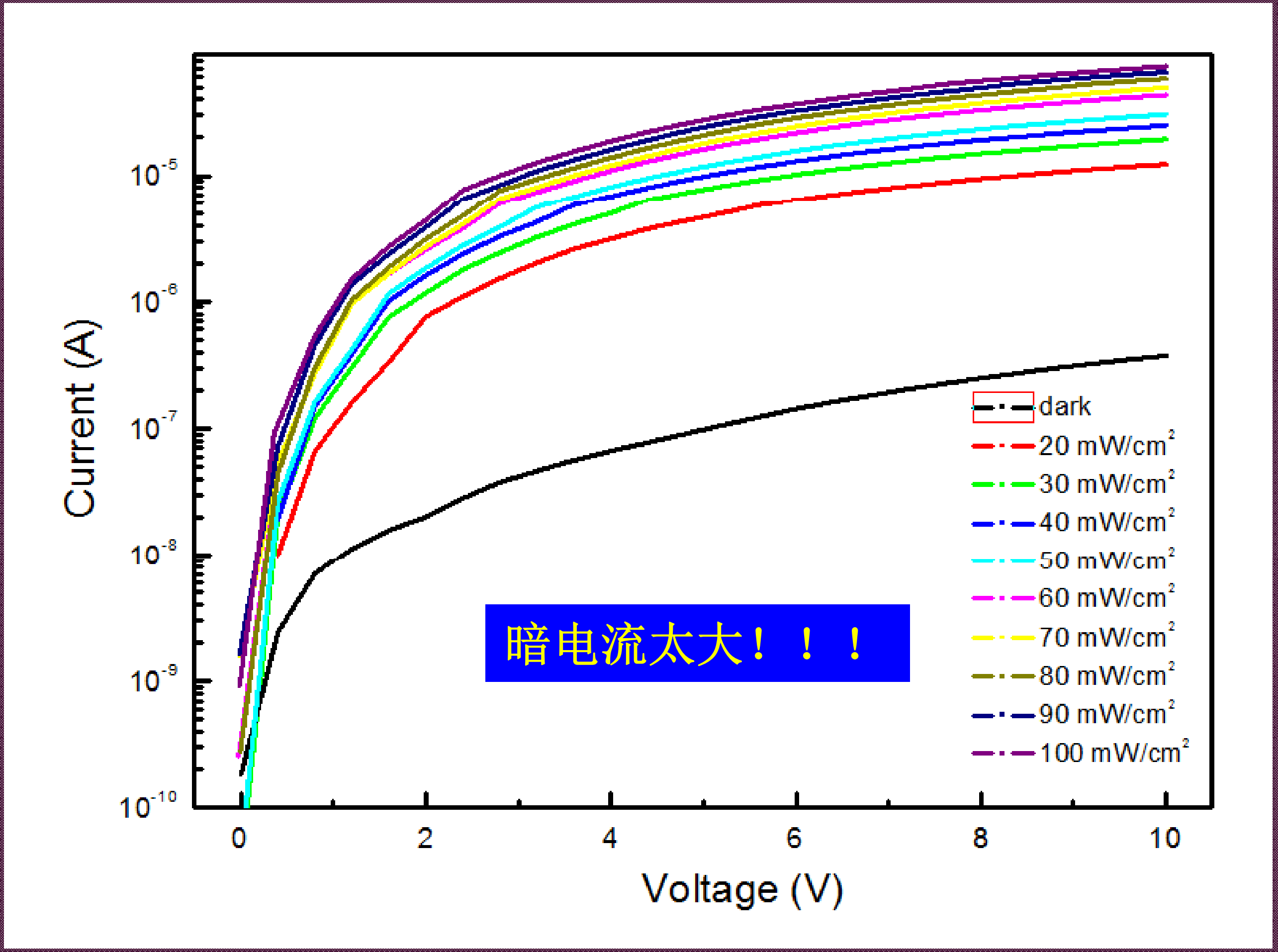
Biexponential fits :
Fast (3.68ns) surface component
slow (30.6ns) bulk component

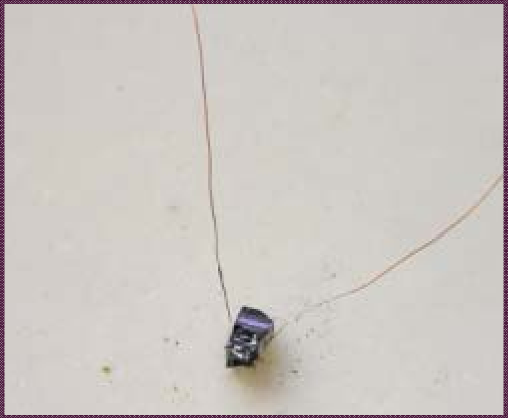


Equation	y = y0 + A1*exp(-(x-x0)/t1) + A2*exp(-(x-x0)/t2)		
Adj. R-Squar	0.99445		
		Value	Standard Err
C	y0	0.00249	0.00104
C	x0	82.6947	--
C	A1	0.25126	--
C	t1	30.6225	2.01472
C	A2	1.13518	--
C	t2	3.68237	0.16768

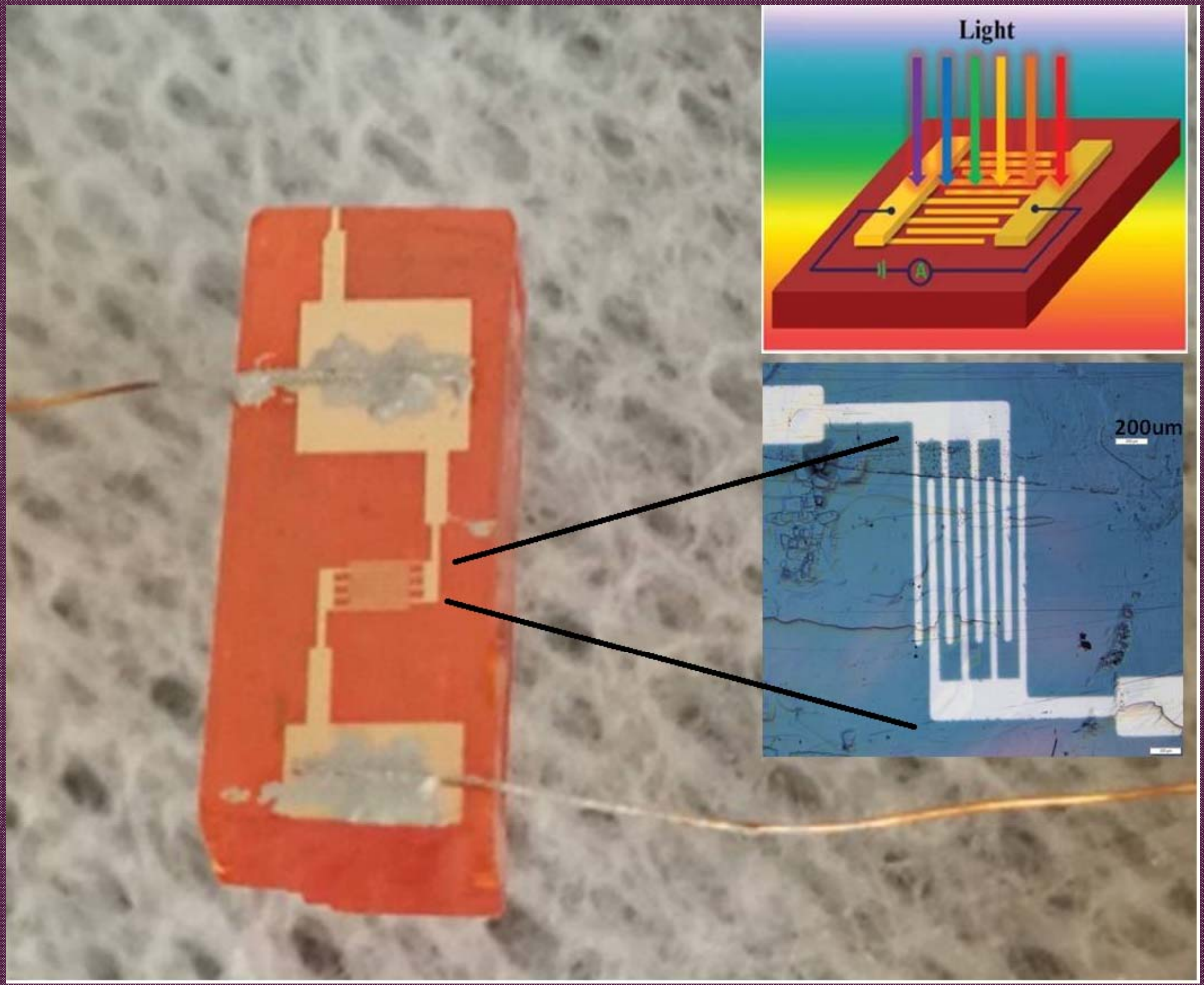
制作探测器





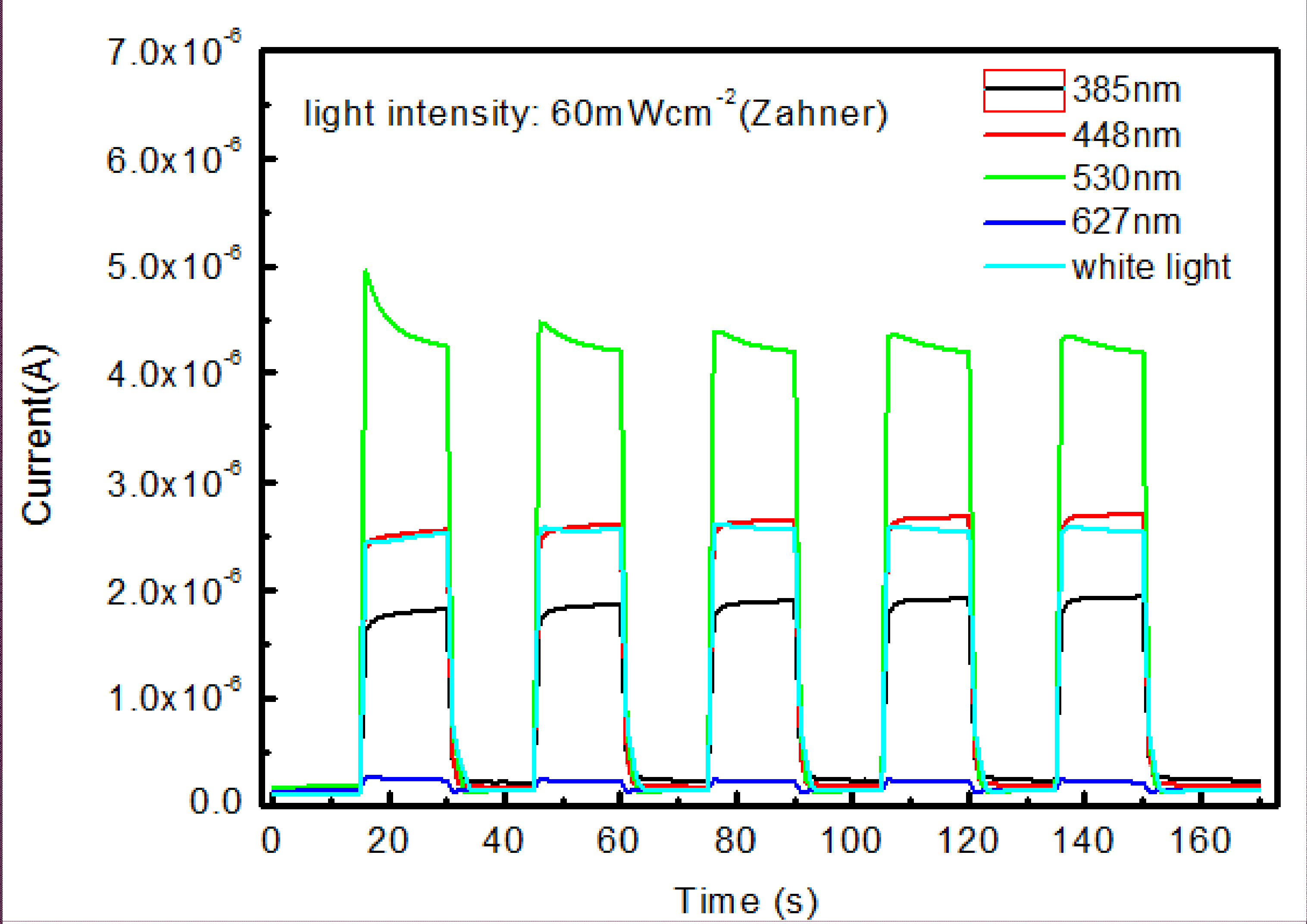


Current-voltage characteristics. Under solar simulator with an intensity of 20-100mW/cm2, the current through a 1mm thick MAPbI3 single crystal photoconductor increases by 33 times.



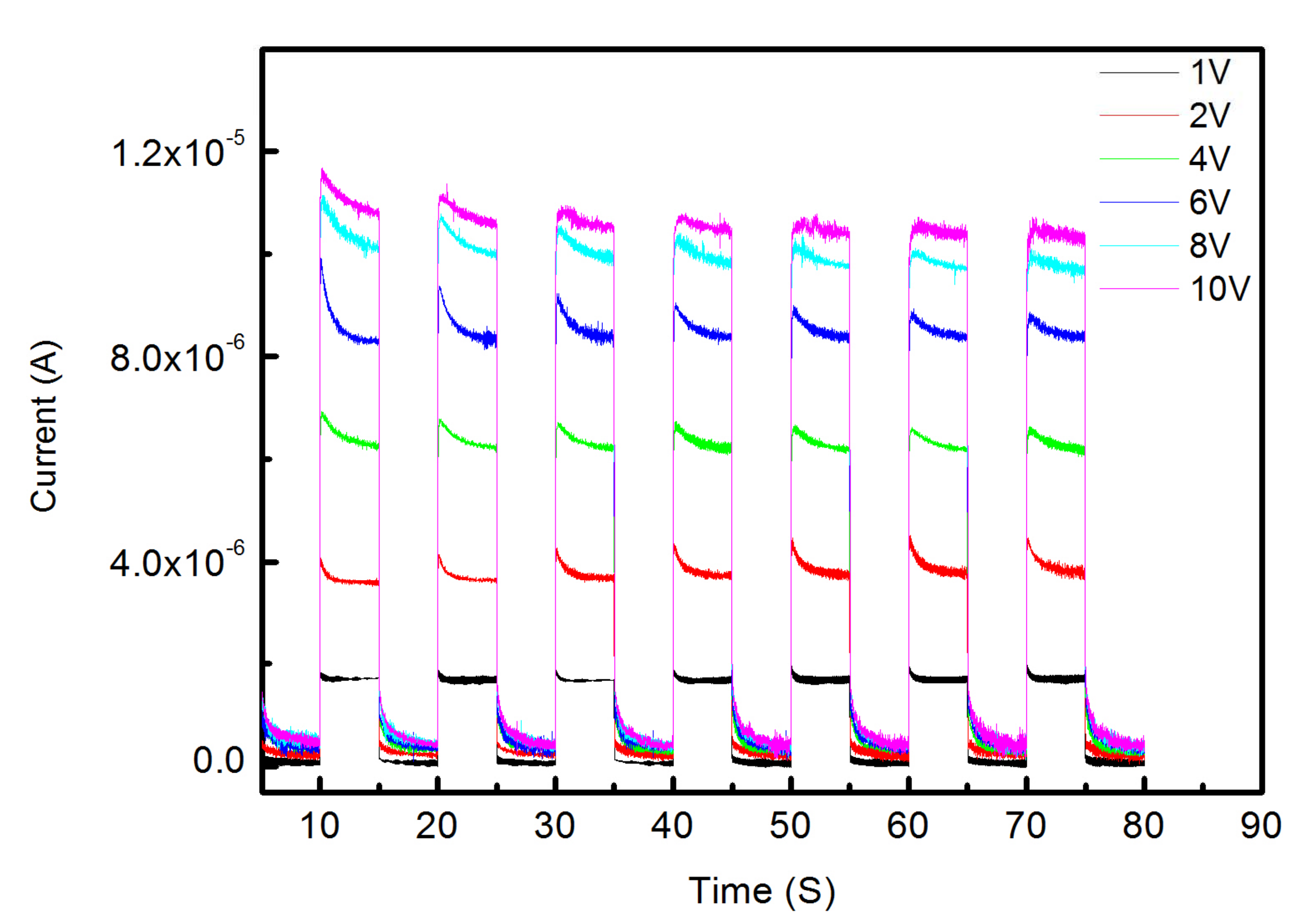
测试： 不同偏压下的光响应
不同光强下的光响应
不同波长下的光响应

不同波长下的光响应

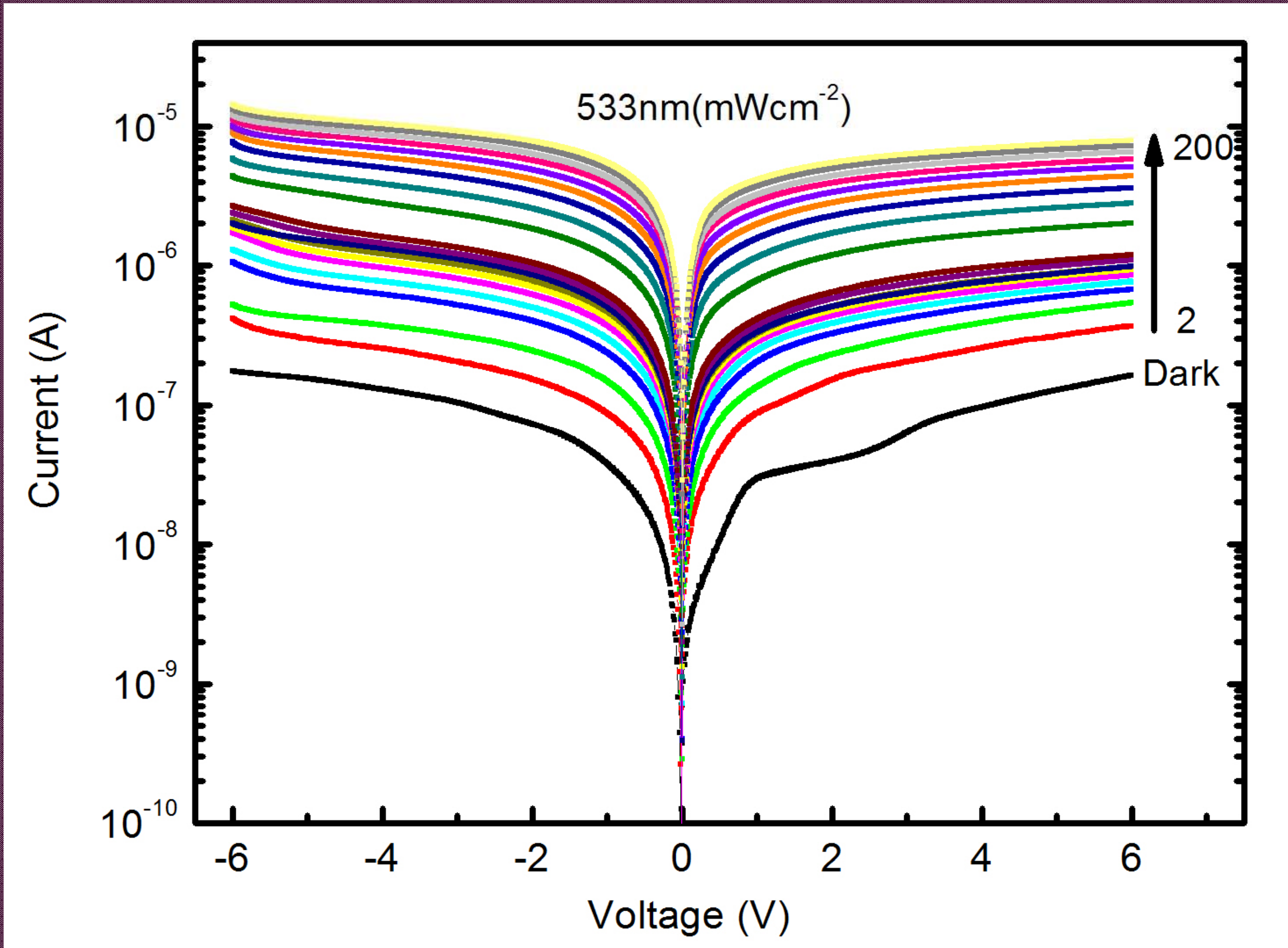


light intensity: 60mWcm^{-2}(Zahner)
385nm
448nm
530nm
627nm
white light
Current(A)
7.0x10^{-6}
6.0x10^{-6}
5.0x10^{-6}
4.0x10^{-6}
3.0x10^{-6}
2.0x10^{-6}
1.0x10^{-6}
0.0
0
20
40
60
80
100
120
140
160
Time (s)

533nm 不同偏压下的光响应

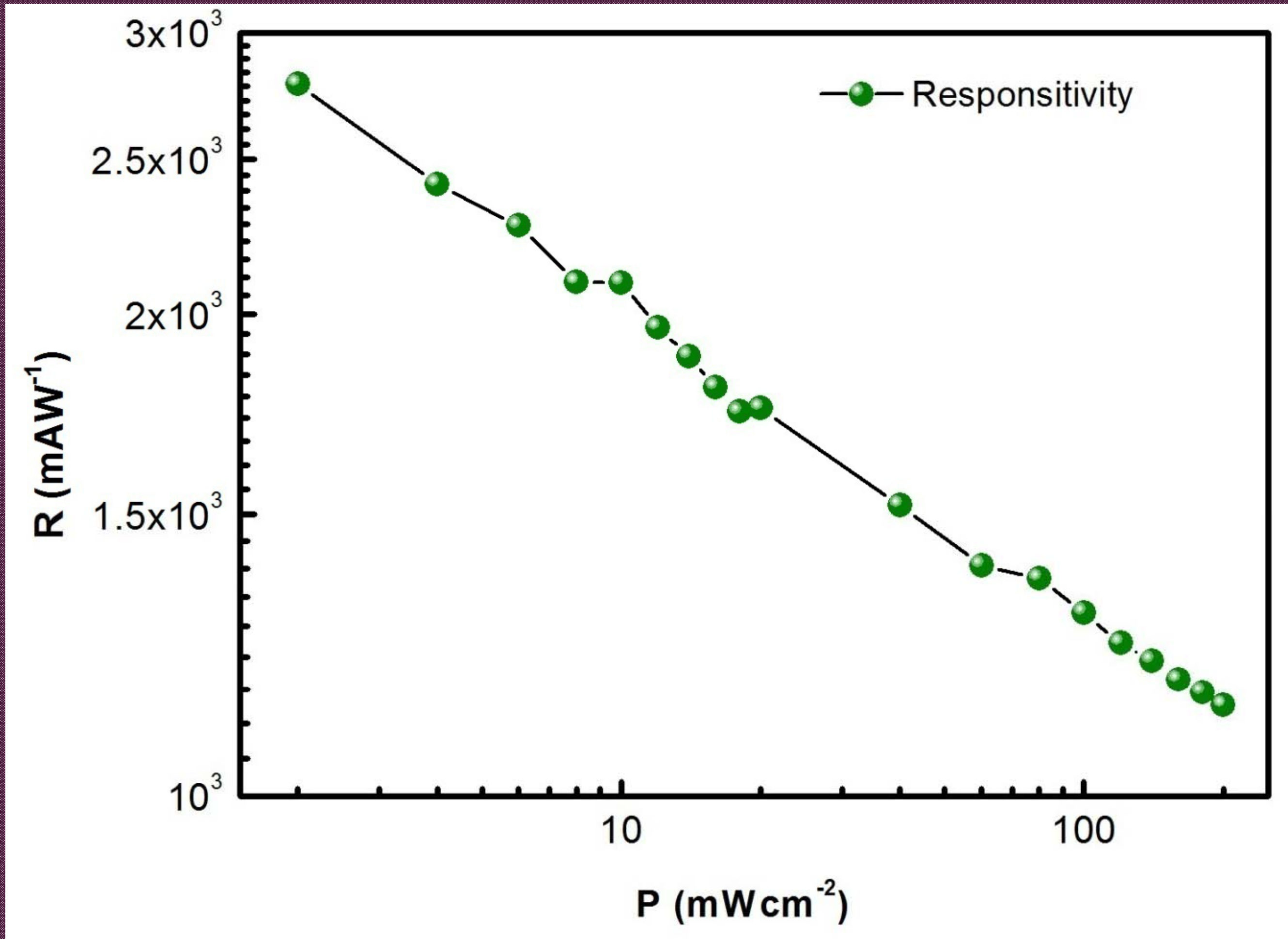


533nm 不同光强下的光响应



灵敏度 Responsivity (R,mAW^{-1}):

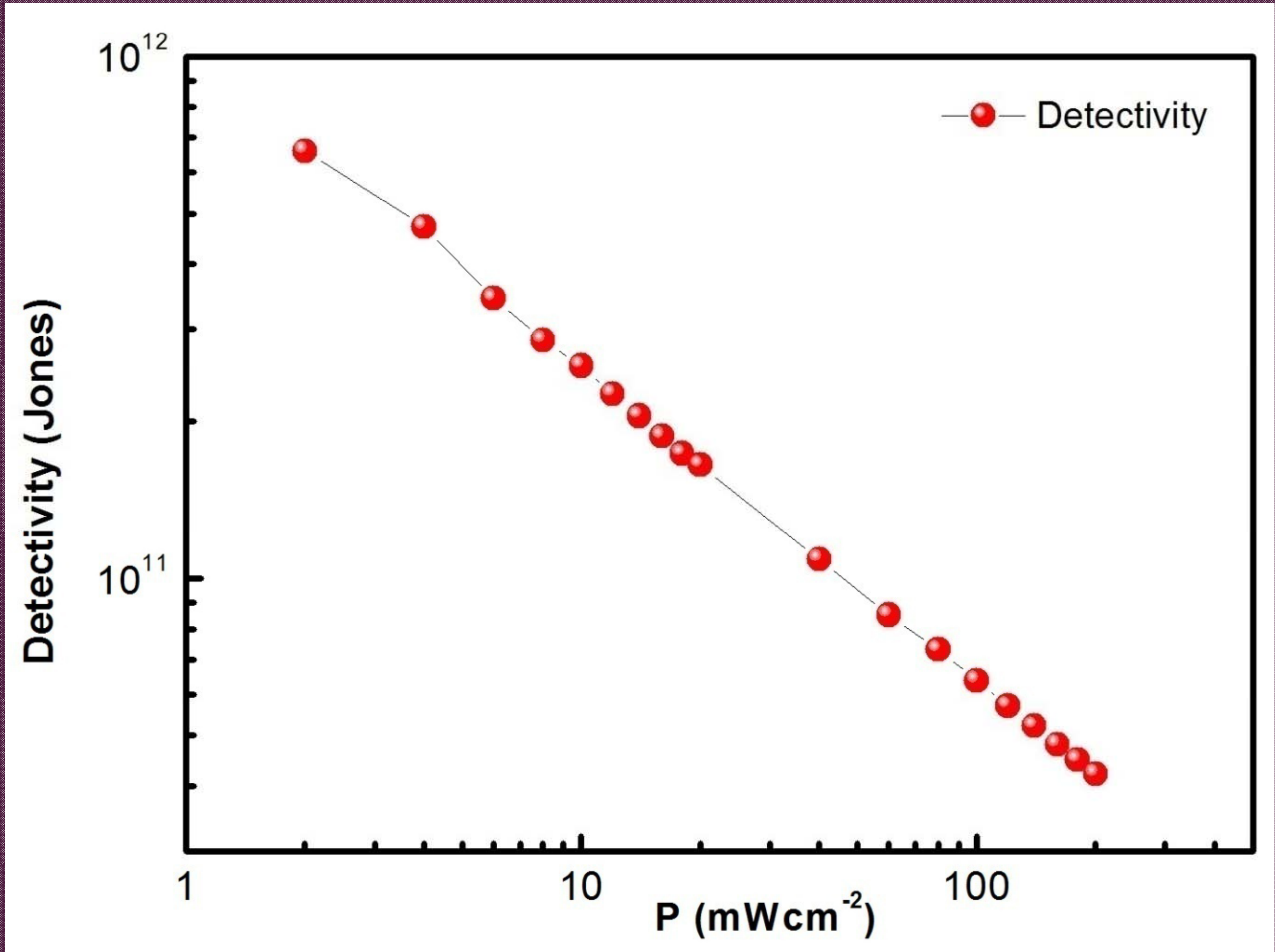
$$R = \frac{J_{ph}}{L_{light}}$$



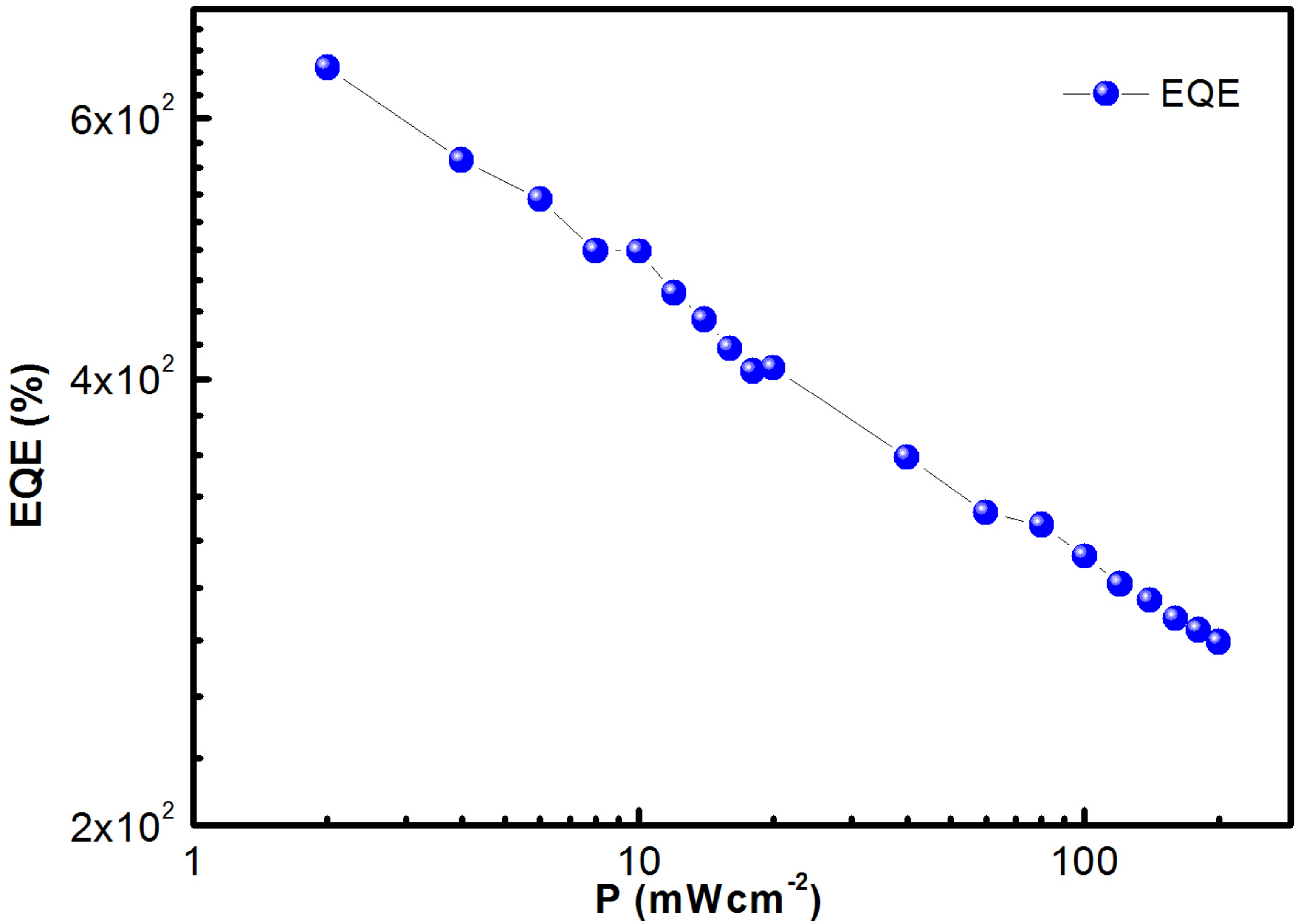
探测度 **Detectivity (D*)**： cmHz$^{1/2}$W^{-1}(Jones)

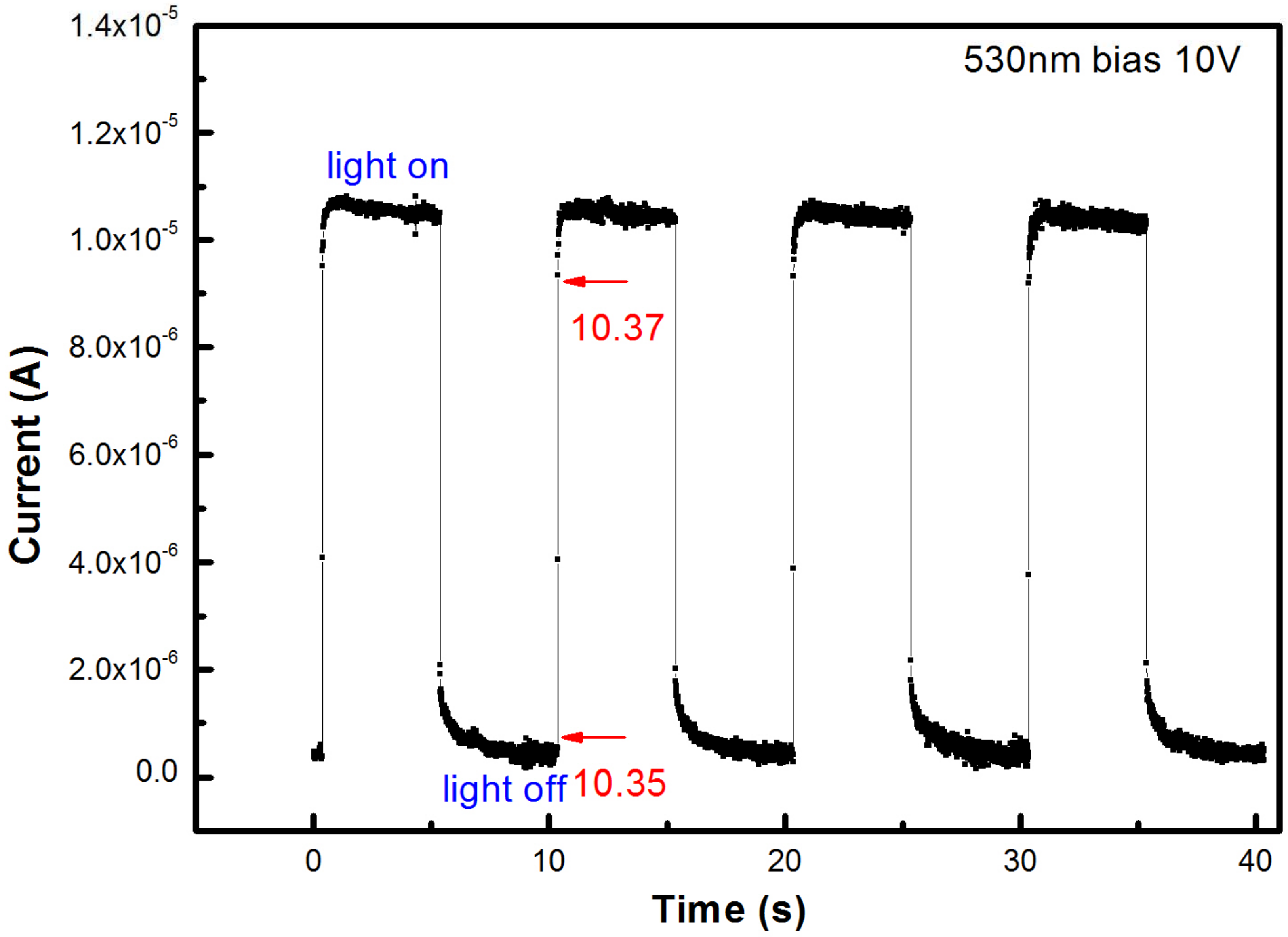
$$D^* = \frac{R}{(2qJ_d)^{1/2}}$$

J_d： the dark current



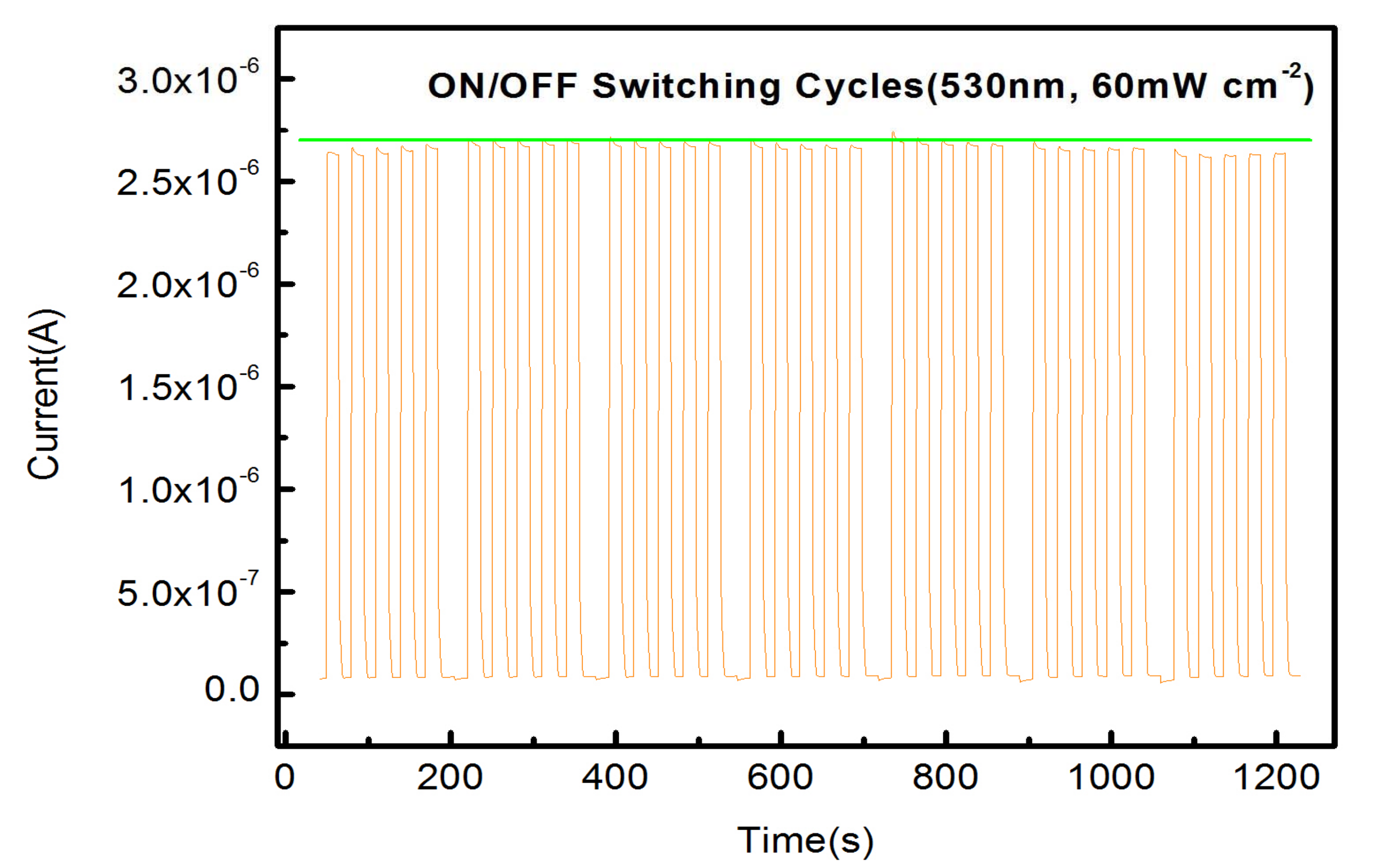
外量子效率（EQE）：%





530nm bias 10V
light on
light off
10.37
10.35
Current (A)
Time (s)
1.4x10-5
1.2x10-5
1.0x10-5
8.0x10-6
6.0x10-6
4.0x10-6
2.0x10-6
0.0
0
10
20
30
40

电化学工作站测试



35 ON/OFF switching cycles of the photocurrent response at a fixed bias voltage of 2 V under illumination (60 mW cm^{-2}, λ = 530 nm).

项 目 总 结

- 利用简单的反温度晶化法和低温温度梯度法可以获得较大尺寸的$MAPbI_3$和$MAPbBr_3$单晶。

- 单晶的组成、光学带隙等与文献一致，且在室温空气中的稳定性良好，可以作为探测器使用。

- 下一步需要寻找合适的表面处理工艺，以降低单晶表面缺陷，提高探测器的灵敏度。

非常感谢重点实验室对本工作的大力支持！

请各位专家批评指正

谢谢！