



南京大學
NANJING UNIVERSITY

基于钙钛矿超构材料的光电探测器研究

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1. 背景
2. 基于钙钛矿超构材料的光电探测器
3. 钙钛矿柔性光电探测器
4. 总结



1. 背景

2. 基于钙钛矿超构材料的光电探测器

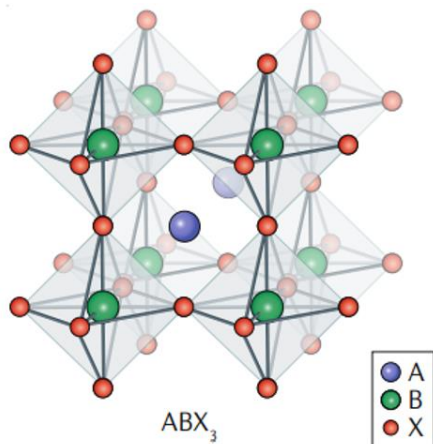
3. 钙钛矿柔性光电探测器

4. 总结



有机-无机杂化钙钛矿材料

□ 金属卤化物钙钛矿：



化学式：ABX₃

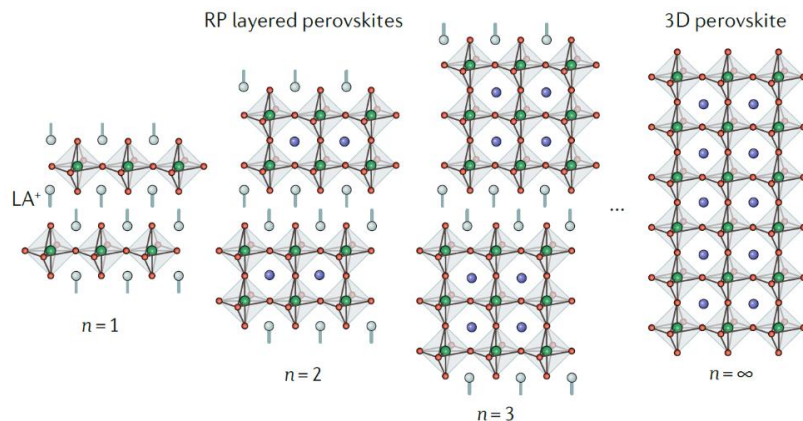
A：MA⁺/FA⁺/Cs⁺...

B：Pb²⁺/Sn²⁺

X：Cl⁻/Br⁻/I⁻

A为有机阳离子时，被称为
有机-无机杂化钙钛矿

□ 二维层状有机-无机杂化钙钛矿：



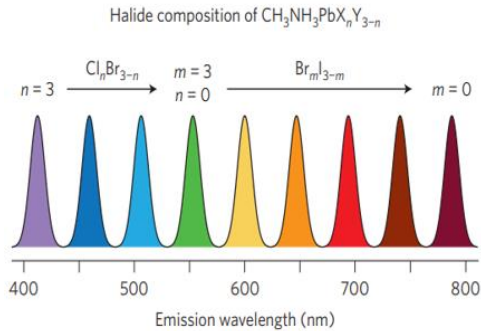
Y. Fu et al., Nat. Rev. Mater. 4, 169 (2019)

2D层状钙钛矿

二维层状有机-无机杂化
钙钛矿的八面体夹在长链
的有机阳离子之间形成多
量子阱结构

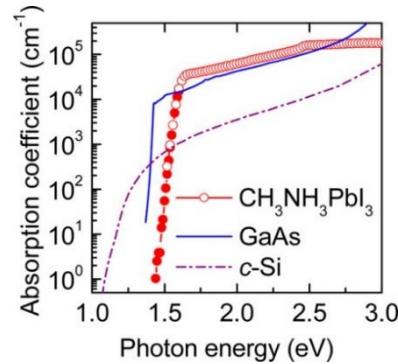
有机-无机杂化钙钛矿的光电学特性

可调的发光波长



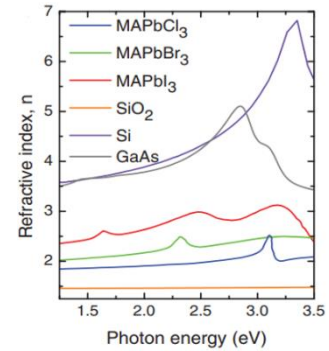
B. R. Sutherland et al., Nat. Photon. 10, 295 (2016)

高吸收系数



S. D. Wolf et al., J. Phys. Chem. Lett. 5, 1035 (2014)

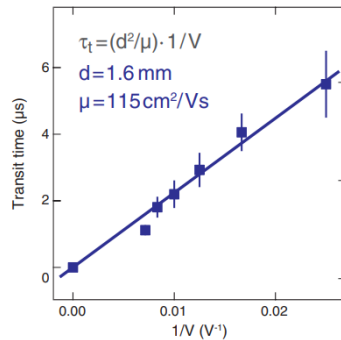
高折射率



S. Makarov et al., Adv. Optical Mater. 7, 1800784 (2019)

高载流子迁移率

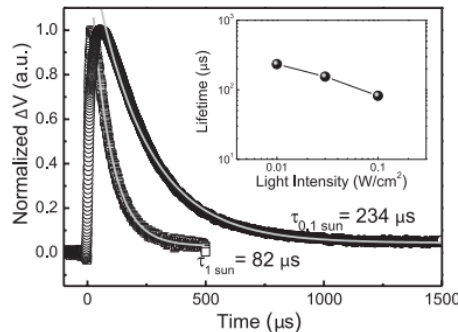
$$\mu = \frac{q\tau}{m^*}$$



D. Shi et al, Science 347, 519 (2015)

长载流子寿命

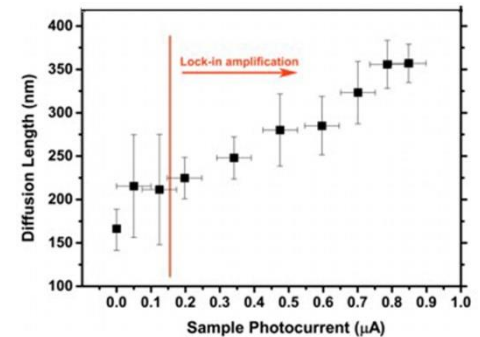
$$\frac{1}{\tau} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}}$$



Q. Dong, et al. Science. 347, 967 (2015)

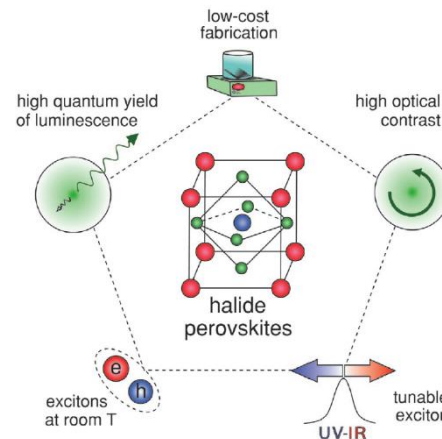
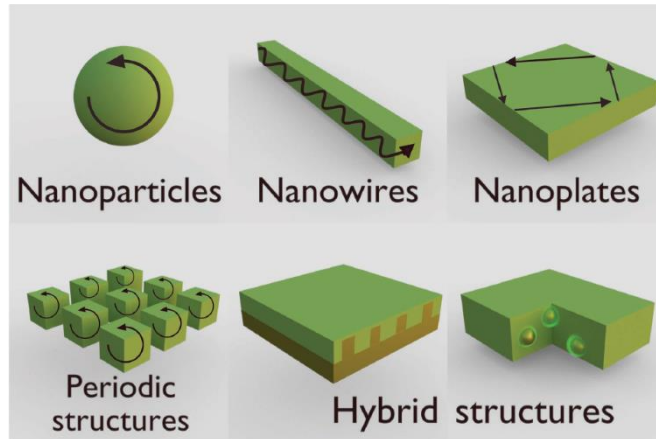
长载流子扩散距离

$$L_D = \sqrt{kT \frac{\mu\tau}{q}}$$



N. Kedem, et al. J. Phys. Chem. Lett. 6, 2469 (2015)

基于钙钛矿材料的纳米结构



纳米结构
共振效应

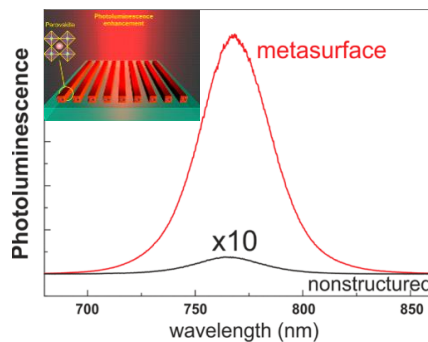


钙钛矿的光
电学特性

S. Makarov et al., Adv. Optical Mater. 7, 1800784 (2019)

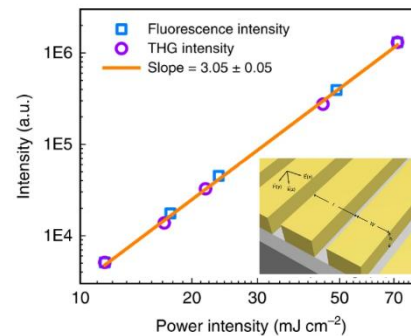
□ 钙钛矿超构表面：

荧光增强



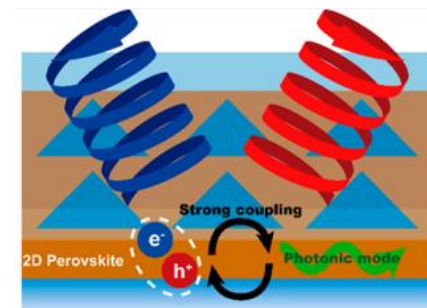
S. V. Makarov et al., ACS Photonics 4, 728 (2017)

三次谐波产生



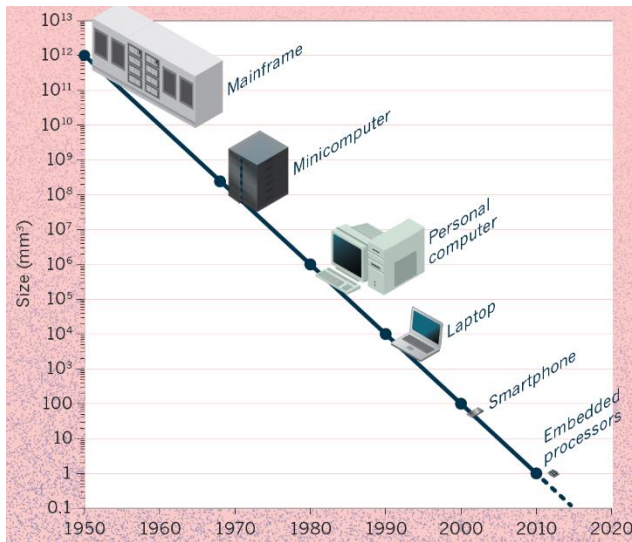
Y. Fan et al., Nat. Commun.10, 2085 (2019)

光子和激子强耦合



S. Kim et al., Nano Lett. 21, 10076 (2021)

基于钙钛矿材料的光电探测



M. M. Waldrop, Nature News 530, 144 (2016)

器件小型化和集成化

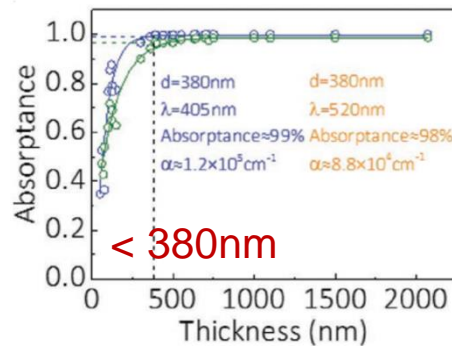


减小器件活性层
(active layer)厚度

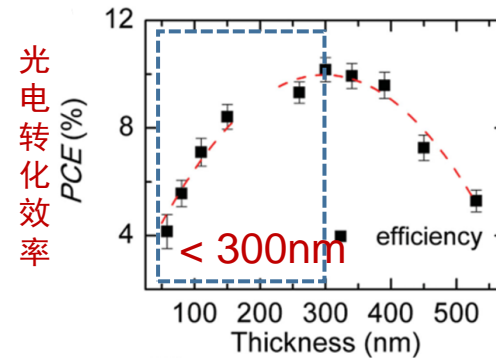


吸收率及光电转化效率降低

□ 钙钛矿活性层厚度对光电器件性能的影响:



Z. Yang et al., Adv. Mater. 8, 1704333 (2018)

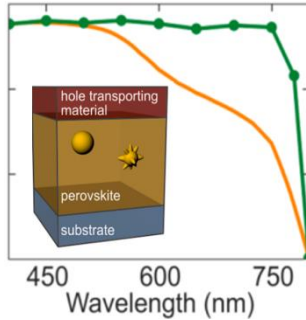


B. Zhang et al., Adv. Mater. Interfaces 3, 1600327 (2016)

增强基于钙钛矿材料的光吸收性能

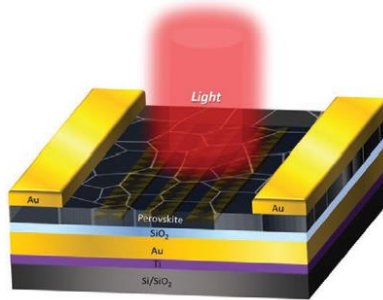
金属纳米结构:

纳米颗粒



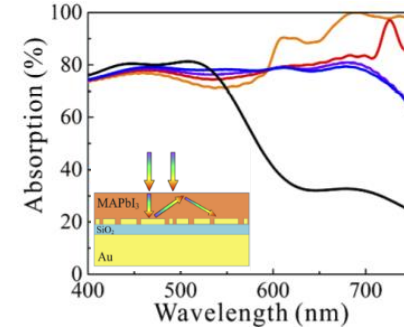
S. C. Palacios et al., ACS Energy Lett. 1, 323 (2016)

等离激元结构



B. Wang et al., Small 16, 2001417 (2020)

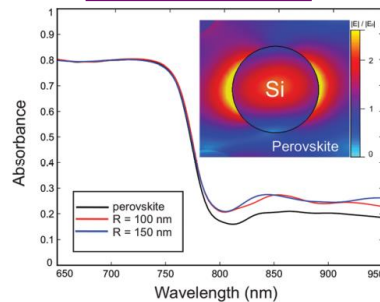
等离激元超构表面



J. He et al., Optics Express 29, 19170 (2021)

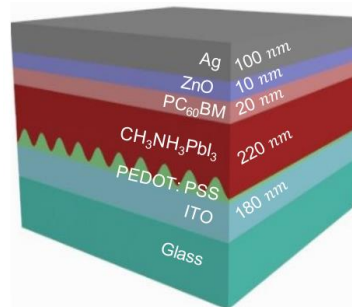
低损耗的介质结构:

Mie共振



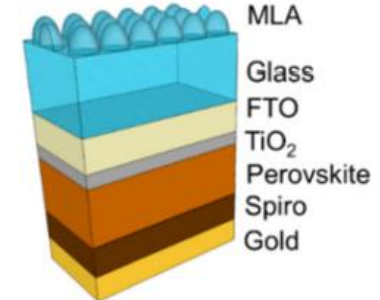
E. Tiguntseva et al., Nanoscale 9, 12486 (2017).

散射结构



N. Li et al., J. Mater. Chem. C. 7, 9573 (2019)

透镜结构



A. Peer et al., Optics Express 25, 10704 (2017)

1. 背景

2. 基于钙钛矿超构材料的光电探测器

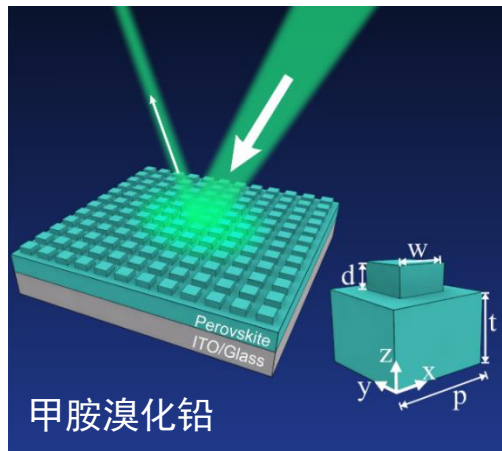
3. 钙钛矿柔性光电探测器

4. 总结

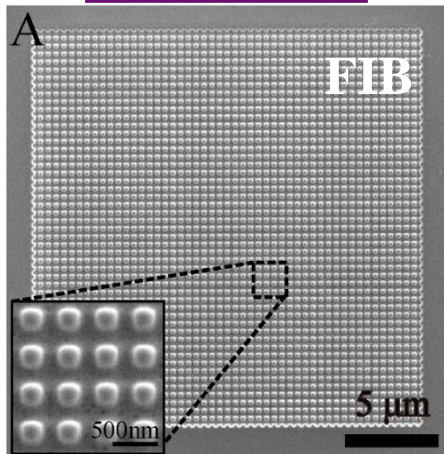


有机-无机杂化钙钛矿超构材料

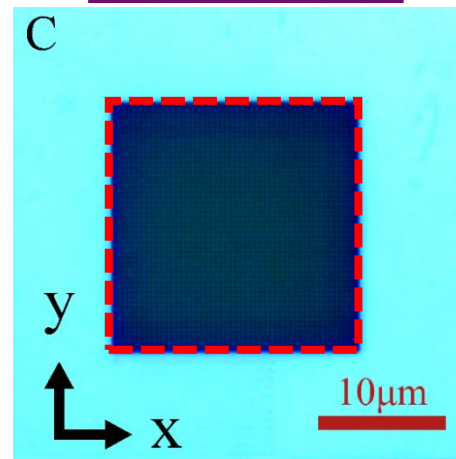
示意图



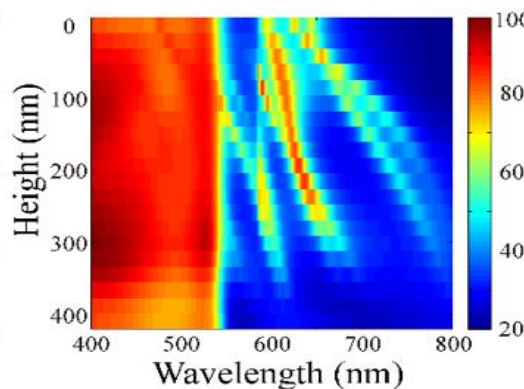
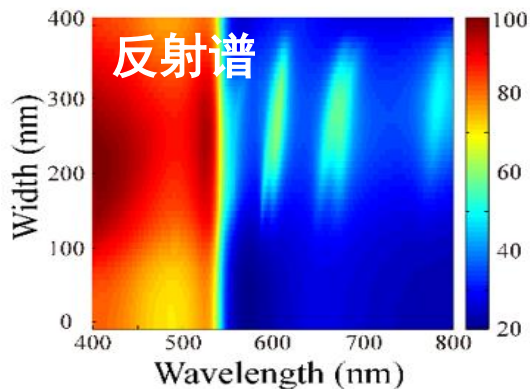
SEM 图像



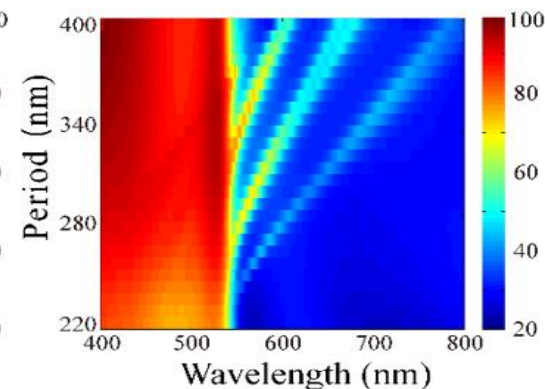
反射图像



Mie 共振模式受共振腔结构参数影响



横向腔模式受周期影响

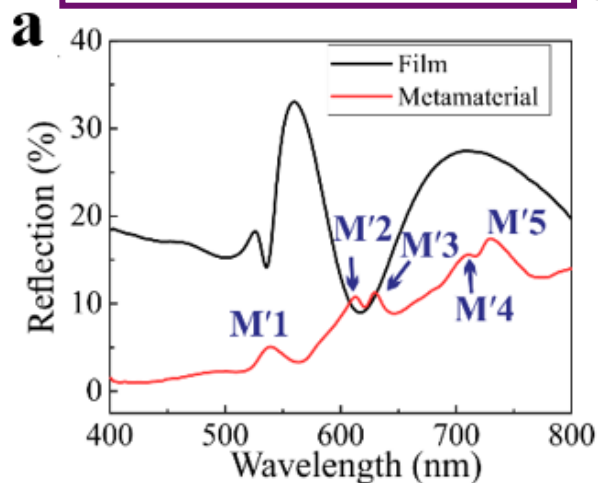


模拟计算优化后结构参数: $w=400$ nm, $d=110$ nm, $t=290$ nm, $p=400$ nm

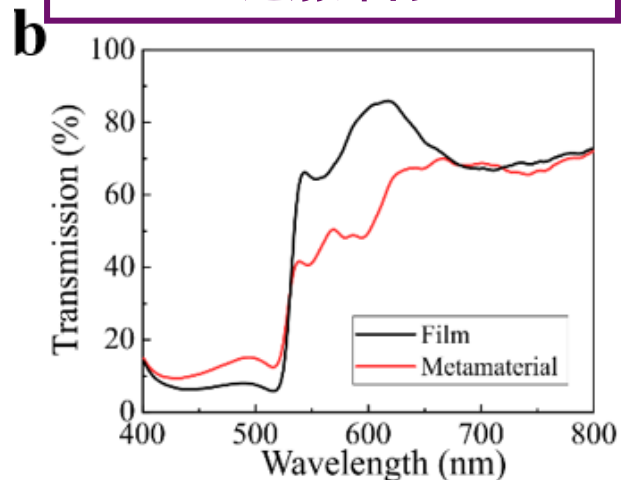
H. Jing et al., Nanophotonics 9, 3323-3333 (2020)

有机-无机杂化钙钛矿超构材料的光学响应

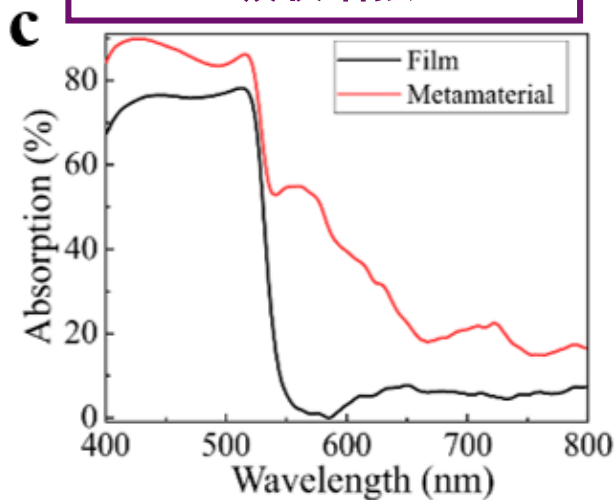
反射抑制



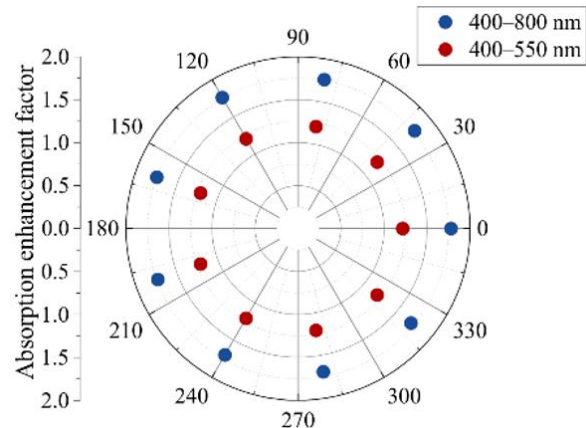
透射抑制



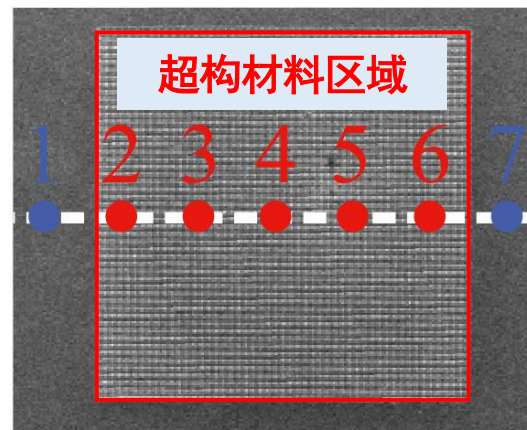
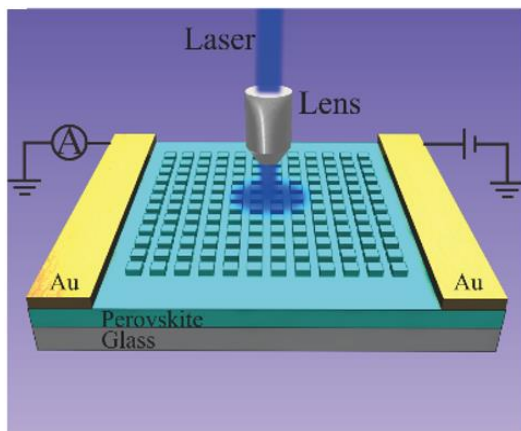
吸收增强



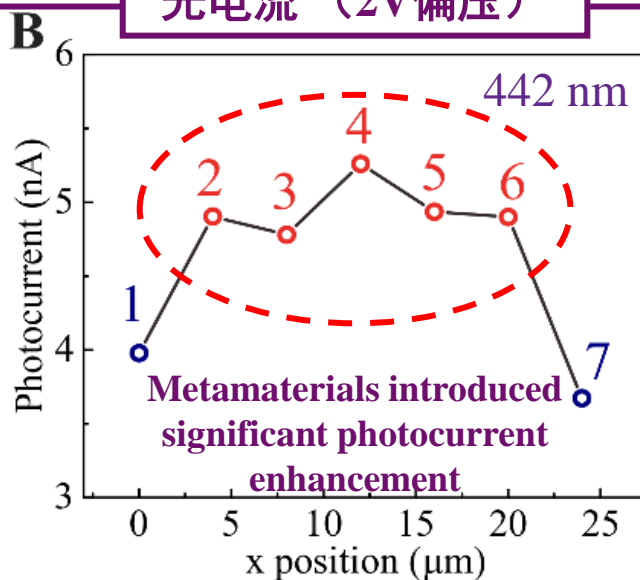
偏振不敏感



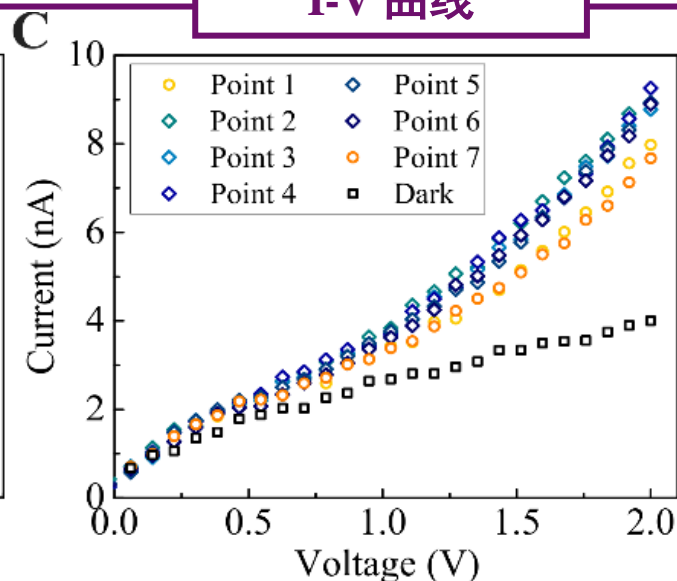
有机-无机杂化钙钛矿超构材料的光电转化特性



光电流 (2V偏压)

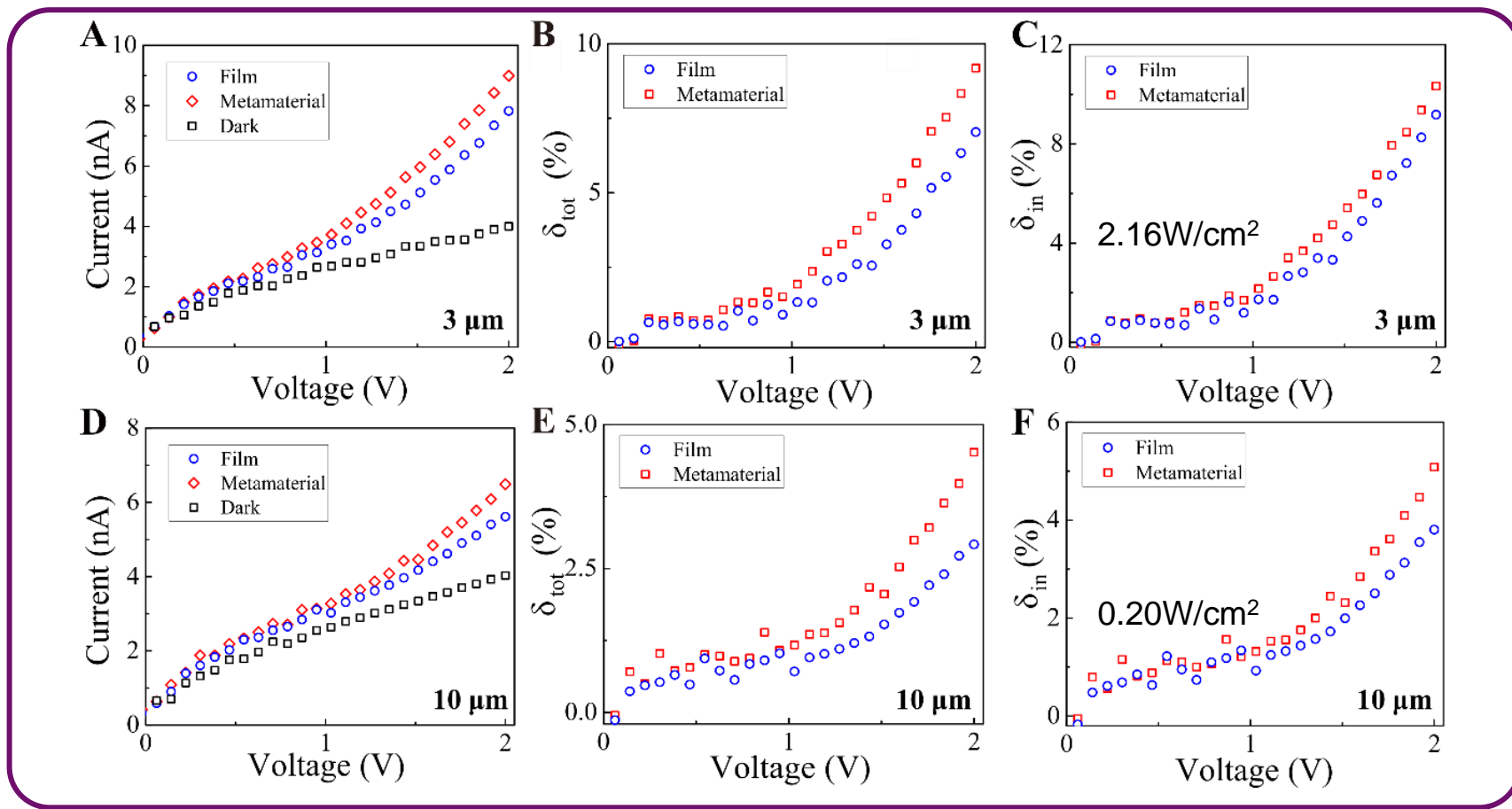


I-V 曲线



H. Jing et al., Nanophotonics 9, 3323-3333 (2020)

有机-无机杂化钙钛矿超构材料的光电转化效率增强



$$\delta_{tot}(\lambda) = \frac{I_{ph}/e}{IS/\frac{hc}{\lambda}} = \frac{I_{ph}}{IS} \frac{hc}{\lambda e}$$

↑ ~39%

有效光生载流子产生效率
单位时间产生的电子比上入射的光子数

光电转化效率增强

↑ ~20%

$$\delta_{in}(\lambda) = \frac{I_{ph}/e}{A(\lambda)IS/\frac{hc}{\lambda}} = \frac{I_{ph}}{A(\lambda)IS} \frac{hc}{\lambda e}$$

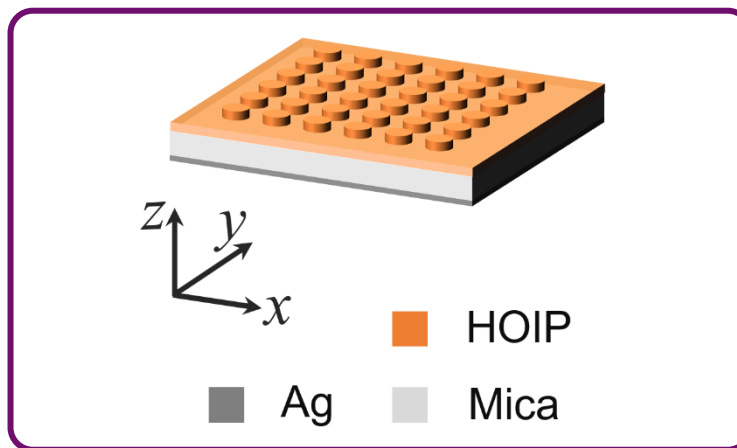
相对内部光生载流子产生效率
单位时间产生的电子比上吸收的光子数

基于钙钛矿超构表面的宽带光电探测器

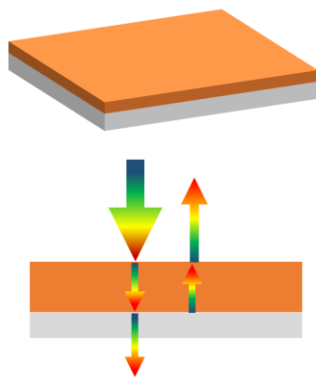
□ 结构示意图及设计原理：

超构表面示意图

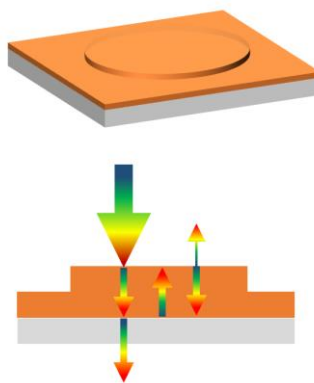
(甲胺碘化铅)



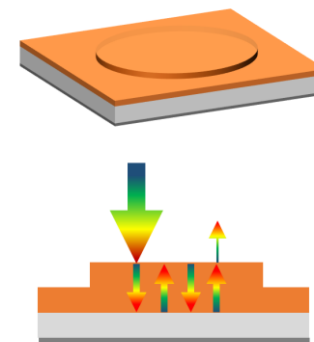
平整薄膜



超构表面



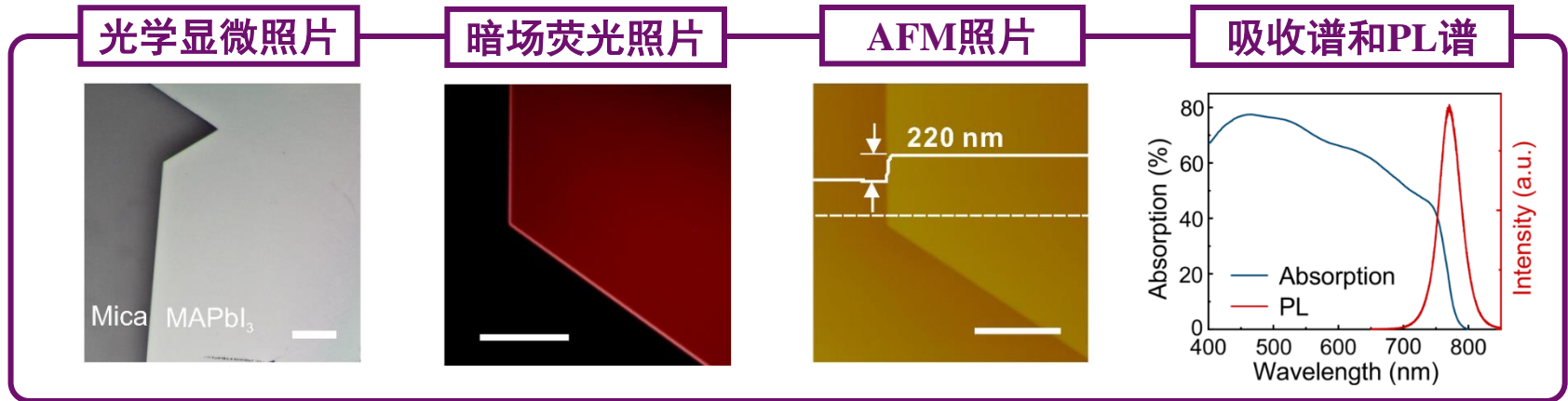
超构表面+反射层



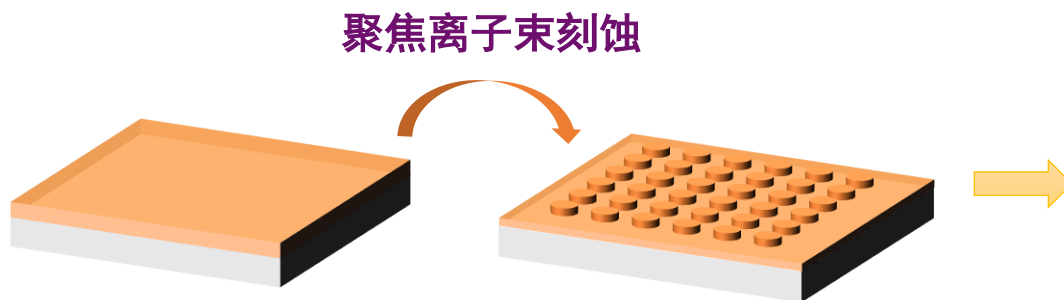
J. He et al., Nano Letters 22, 6655-6663 (2022)

钙钛矿薄膜表征及超构表面制备

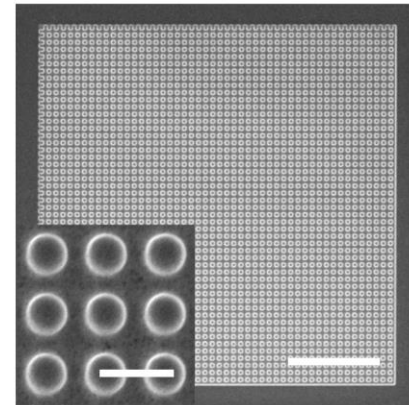
□ 甲胺碘化铅(MAPbI₃)钙钛矿薄膜:



□ 钙钛矿超构表面制备:



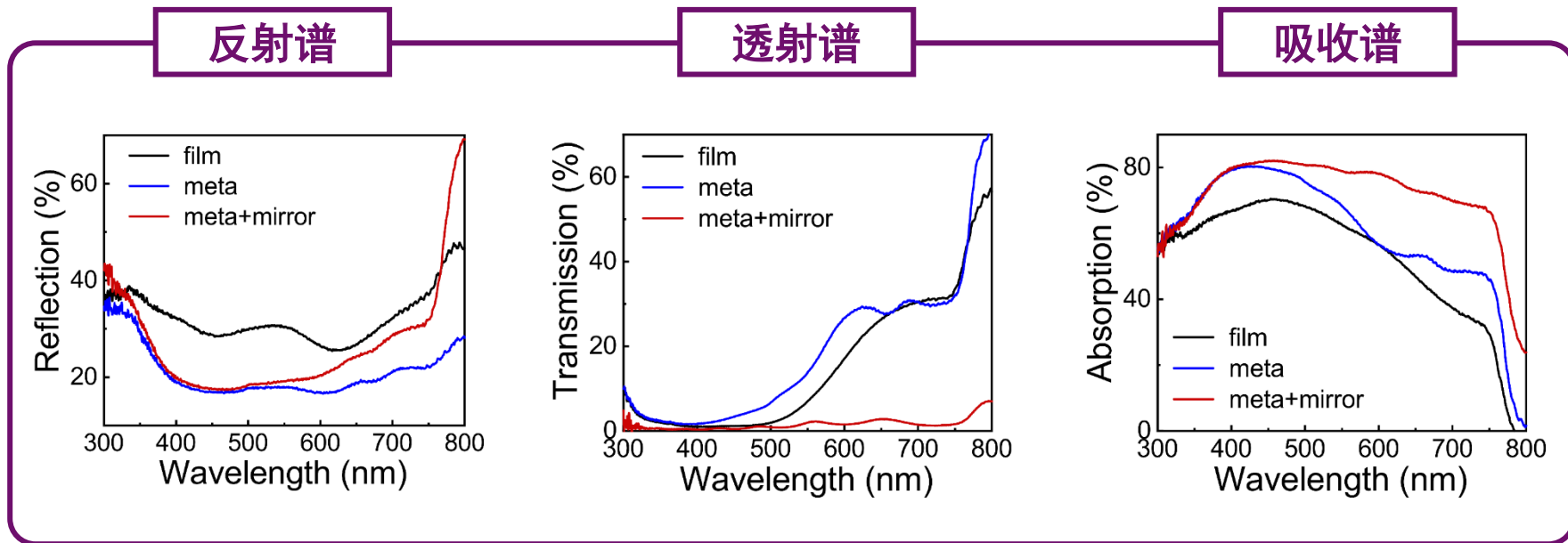
超构表面SEM照片



J. He et al., *Nano Letters* 22, 6655-6663 (2022)

钙钛矿超构表面光学响应

□ 实验测量的光谱：



- ✓ 通过构造钙钛矿超构表面并引入背部反射层，可以实现**宽带吸收增强**的效果

钙钛矿超构表面光电流响应

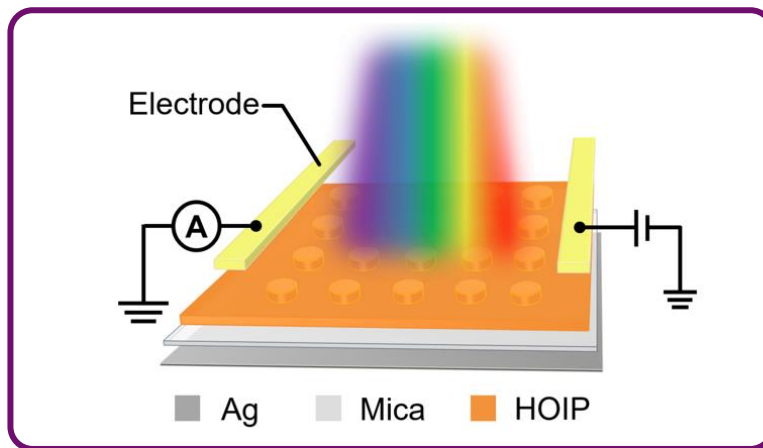
光吸收增强



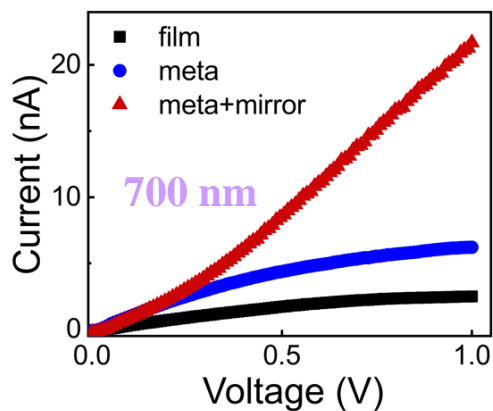
光生载流子数量增加

□ 电学测量:

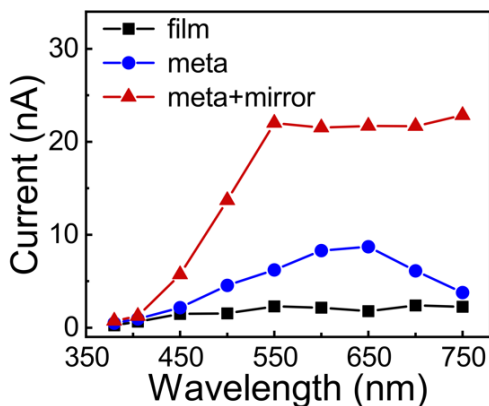
测量装置示意图



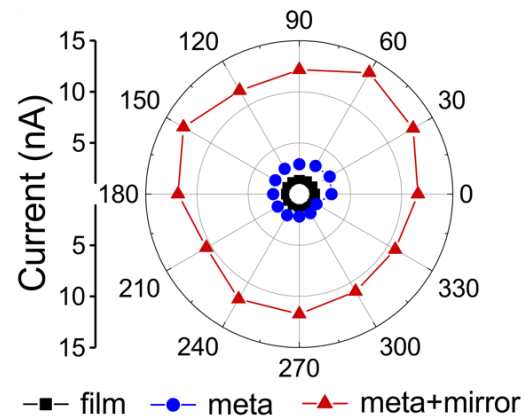
光电流增强(700 nm)



宽带增强

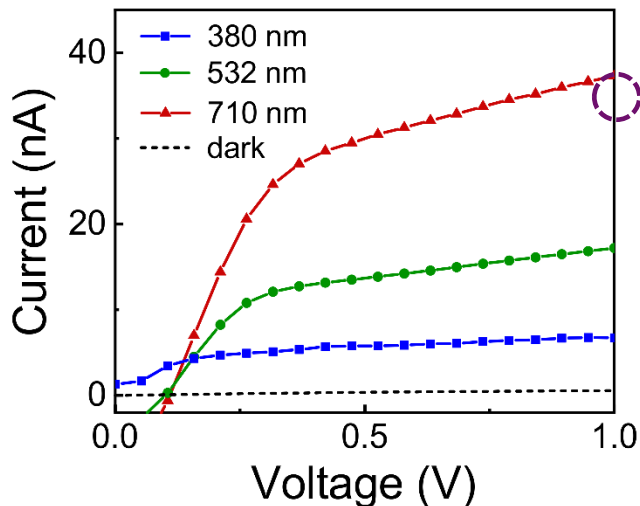


偏振不敏感



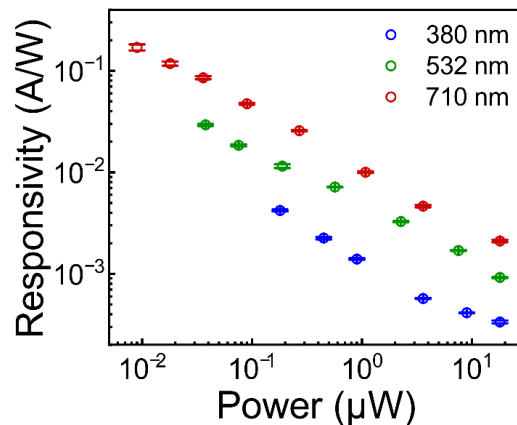
钙钛矿超构表面光电探测器的性能

紫外和可见光照射下的I-V曲线



710 nm@1 V时，光电流为38 nA，暗电流为0.55 nA，此时光电探测器的开关比约为70

响应率



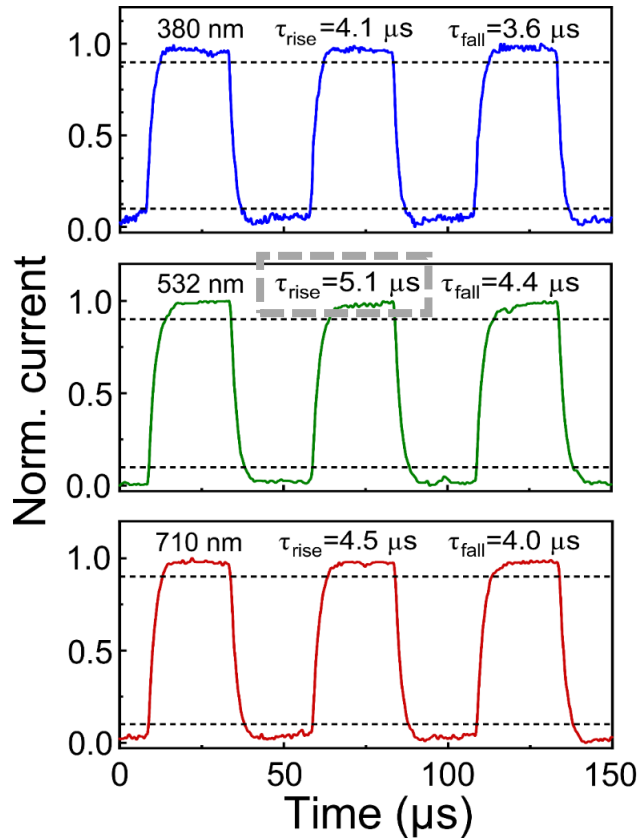
$$R = \frac{I_{photo} - I_{dark}}{P_{inc}}$$

710 nm: 170 mA/W
532 nm: 30 mA/W
380 nm: 4 mA/W

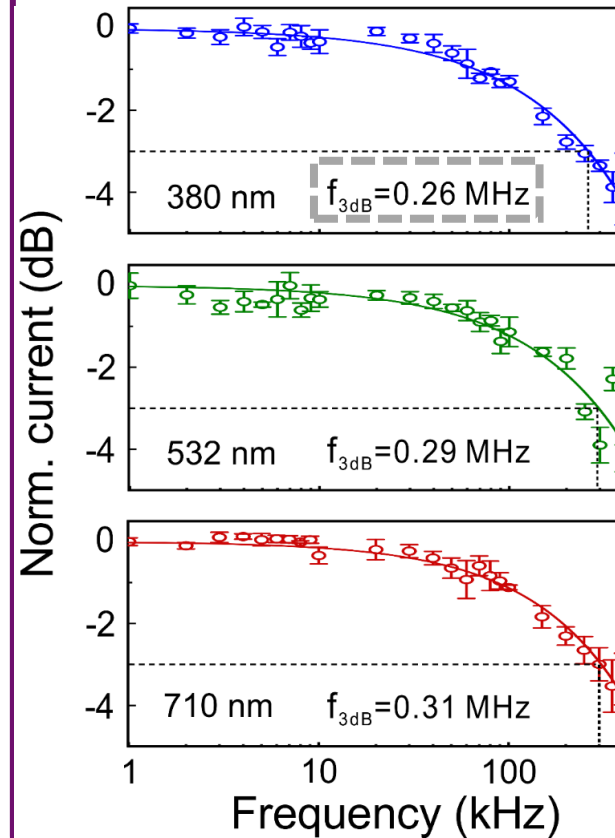
✓ 在紫外和可见光波段的响应率都比较高，跟商用的硅基探测器相当，证实其具有宽带光电探测的能力

钙钛矿超构表面光电探测器的性能

上升/下降时间

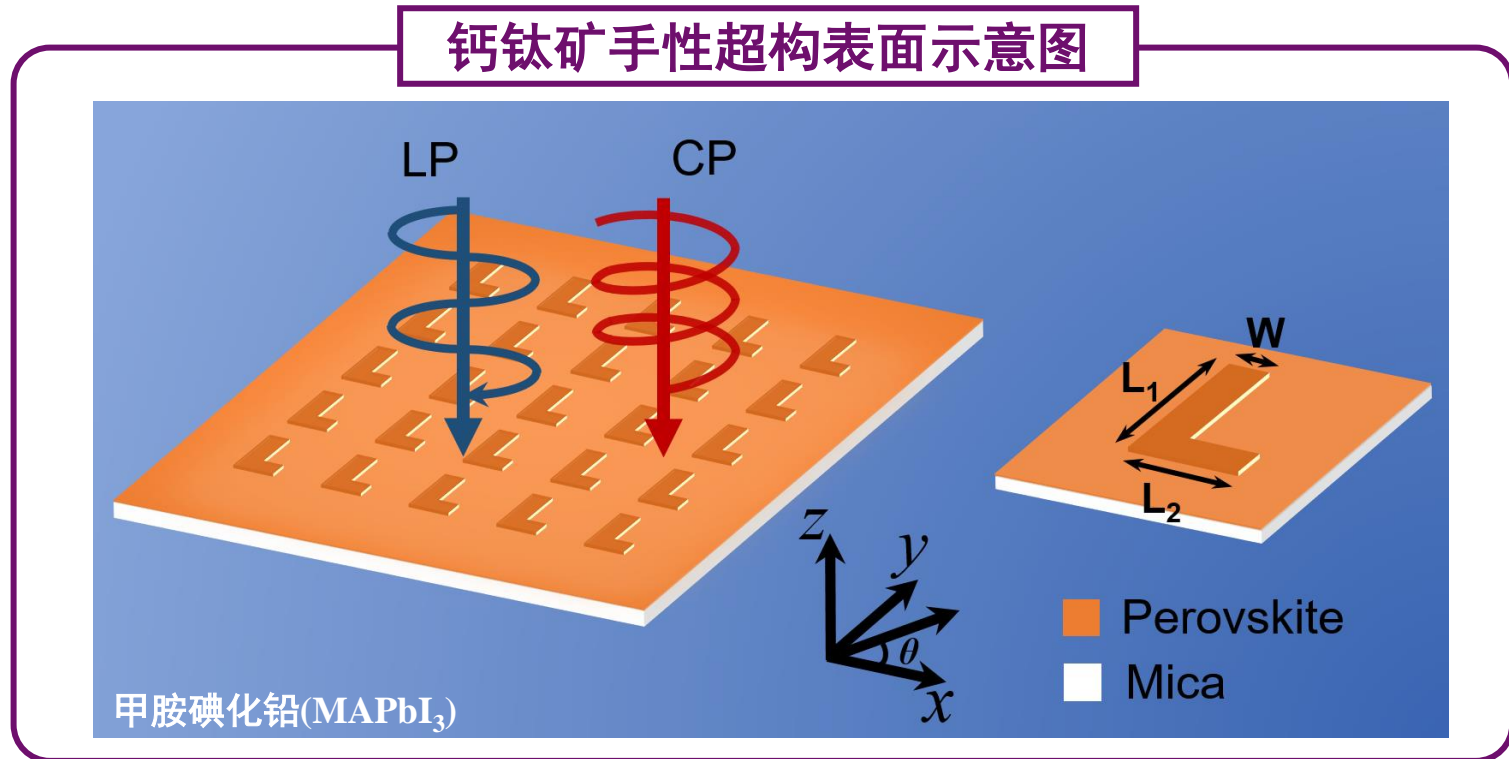


3 dB带宽



✓ 高速的光电探测性能

钙钛矿手性超构表面示意图

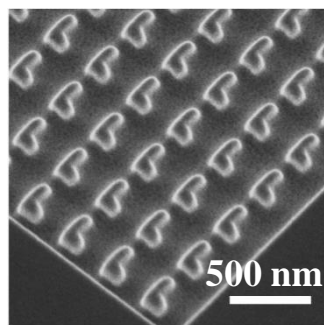
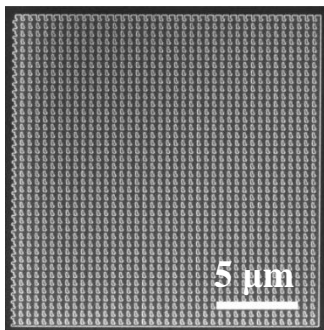


- ✓ 超构表面的天线单元具有**各向异性**，因此对沿x轴和y轴方向偏振的电磁波具有不同的响应；又因为纳米天线**镜面非对称**，故对于左/右旋圆偏振光的响应也会不同。因此可以来设计**多偏振态响应**的光电探测器。

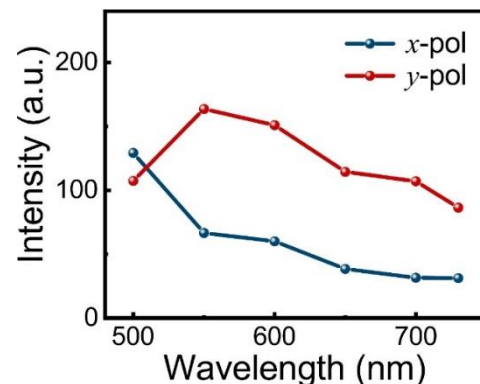
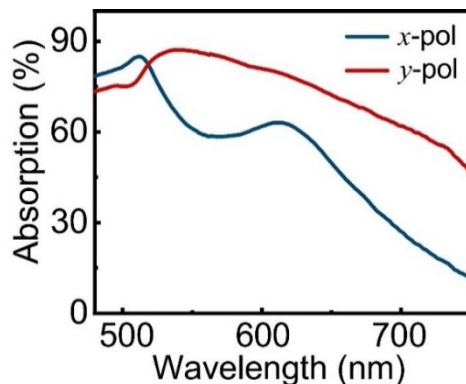
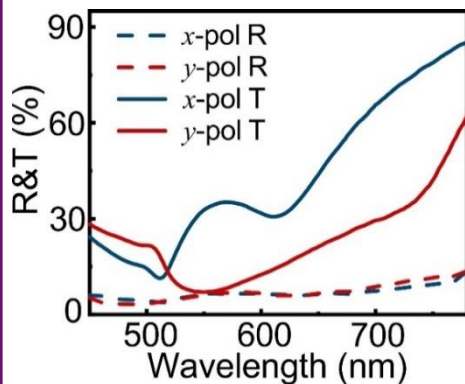
C. Y. Li et al., Optics Letters 47, 565 (2022)

钙钛矿超构表面的光学响应

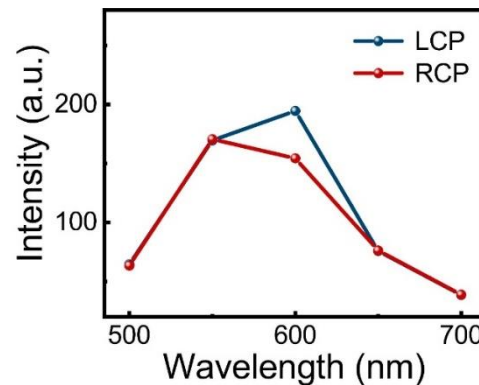
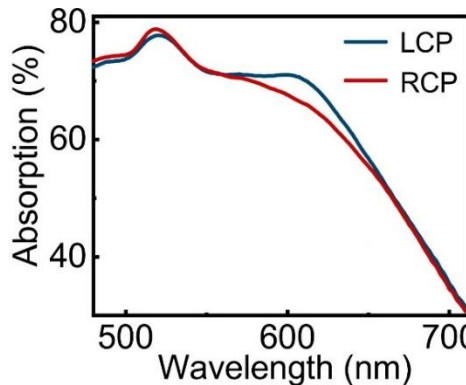
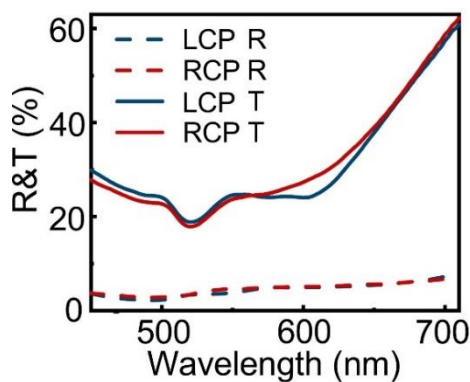
SEM 图像



线偏振



圆偏振



反射和透射谱

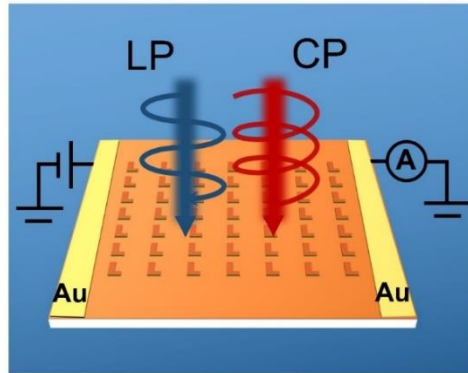
吸收谱

光致发光激发光谱

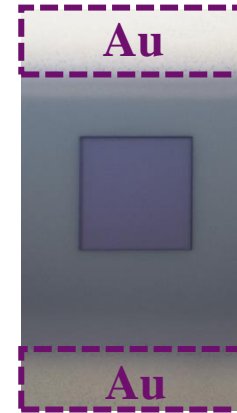
多偏振光电探测器

□ 电学测量:

多偏振光电探测器示意图



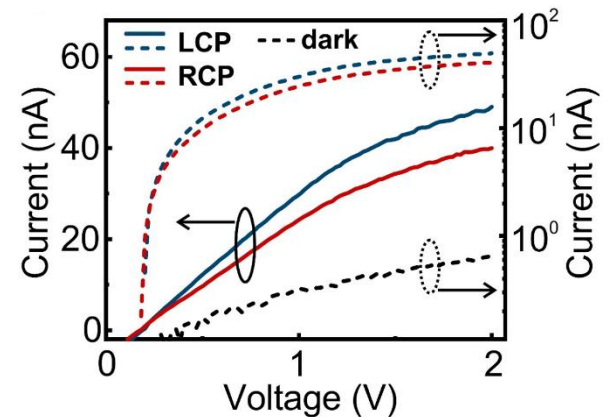
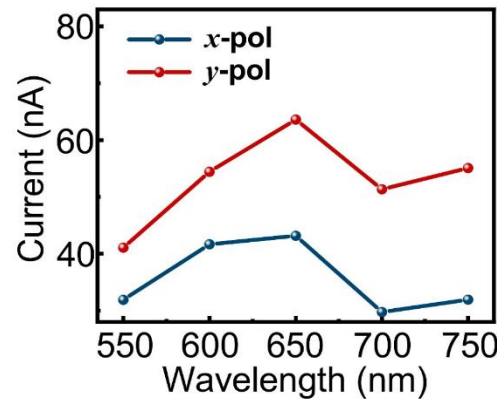
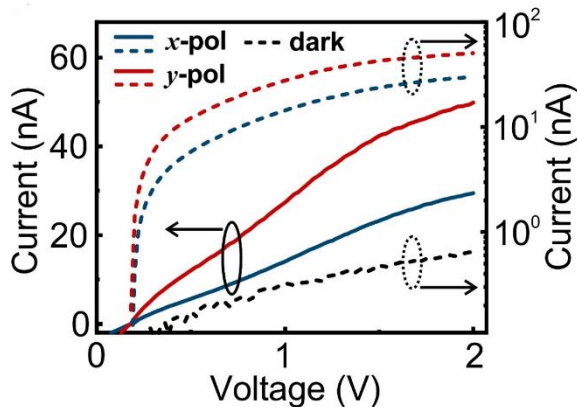
光学显微照片



线偏振

宽带线偏探测

圆偏振

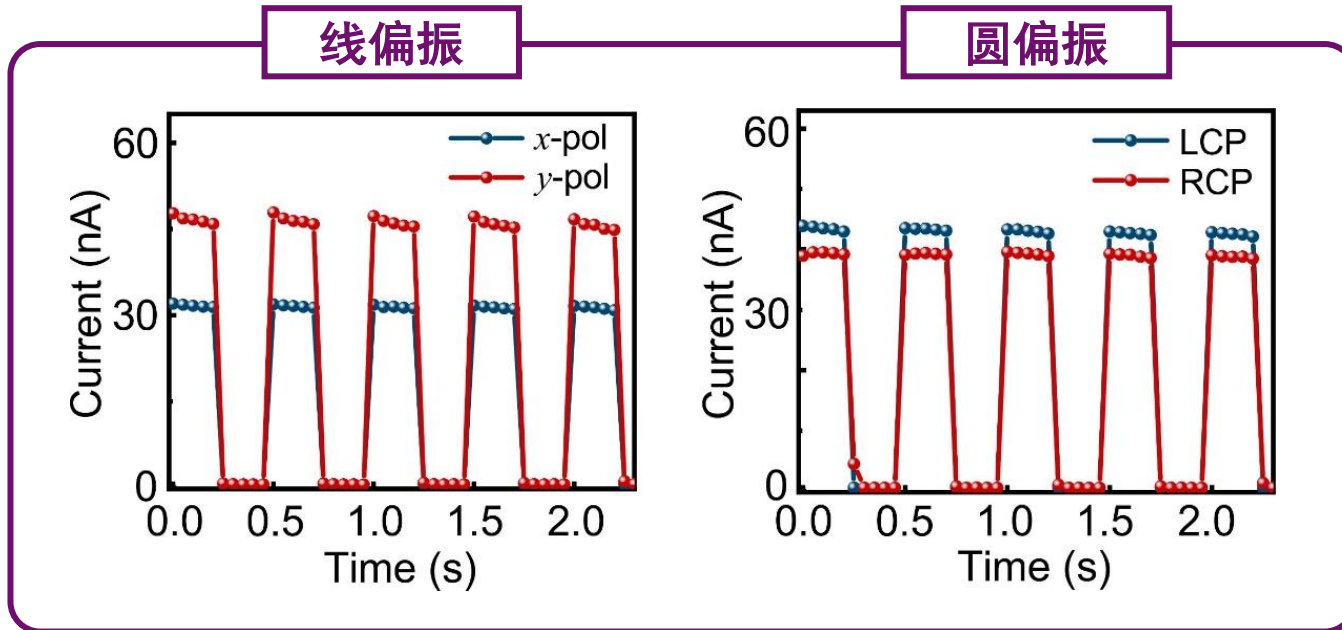


Responsivity: 5mA/W; detectivity: 1.1×10^8 Jones.

C. Y. Li et al., *Optics Letters* 47, 565 (2022)

多偏振光电探测器

□ 时间分辨的光电流响应：



✓ 证实了光电探测器具有多偏振态敏感的光电探测功能

1. 背景

2. 基于钙钛矿超构材料的光电探测器

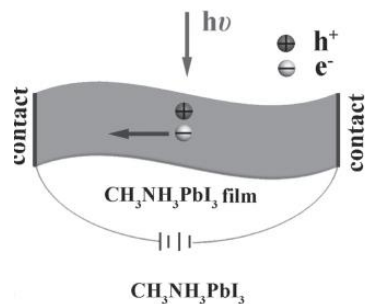
3. 钙钛矿柔性光电探测器

4. 总结



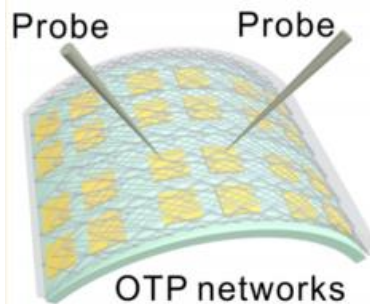
钙钛矿柔性光电探测器背景

薄膜



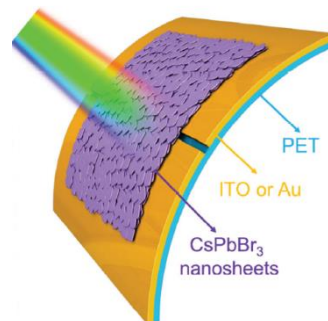
X. Hu et al. Adv. Funct. Mater.
24, 7373 (2014)

纳米线网络



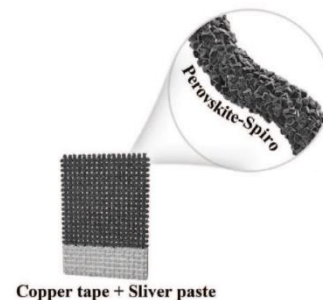
H. Deng et al. Nano Lett.
15, 7963 (2015)

纳米片分散体



J. Song et al. Adv. Mater.
28, 4861 (2016)

纺织物



H. Sun et al. Small
13, 1701042 (2017)

多晶钙钛矿

溶液法制备，与柔性衬底兼容性好

载流子迁移率低、载流子扩散距离短
在空气中稳定性差

单晶钙钛矿

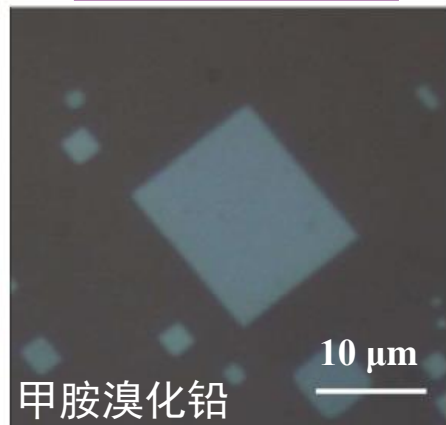
化学气相沉积等，与柔性衬底兼容性差

载流子迁移率高、载流子扩散距离长
在空气中稳定性好

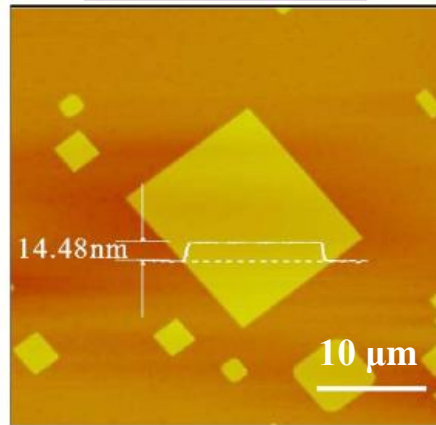
准静态溶液生长法在柔性衬底上制备超薄的单晶钙钛矿薄膜
实现高性能柔性钙钛矿光电探测器

制备的超薄单晶有机-无机杂化钙钛矿纳米片

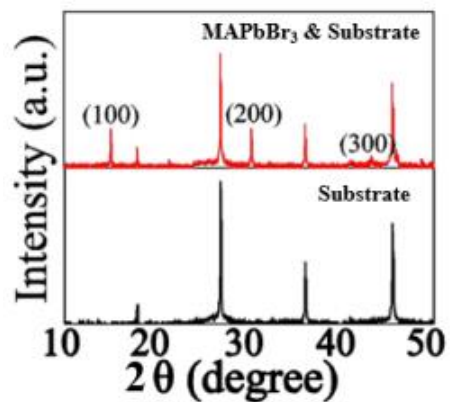
显微光学照片



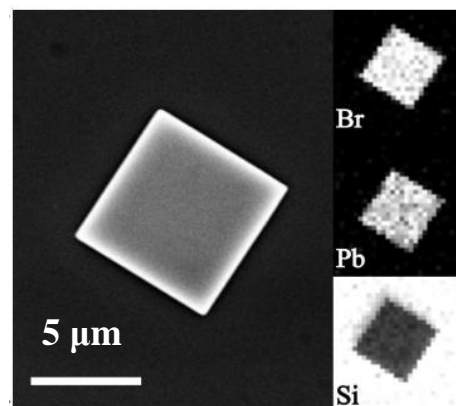
AFM 图像



XRD 谱



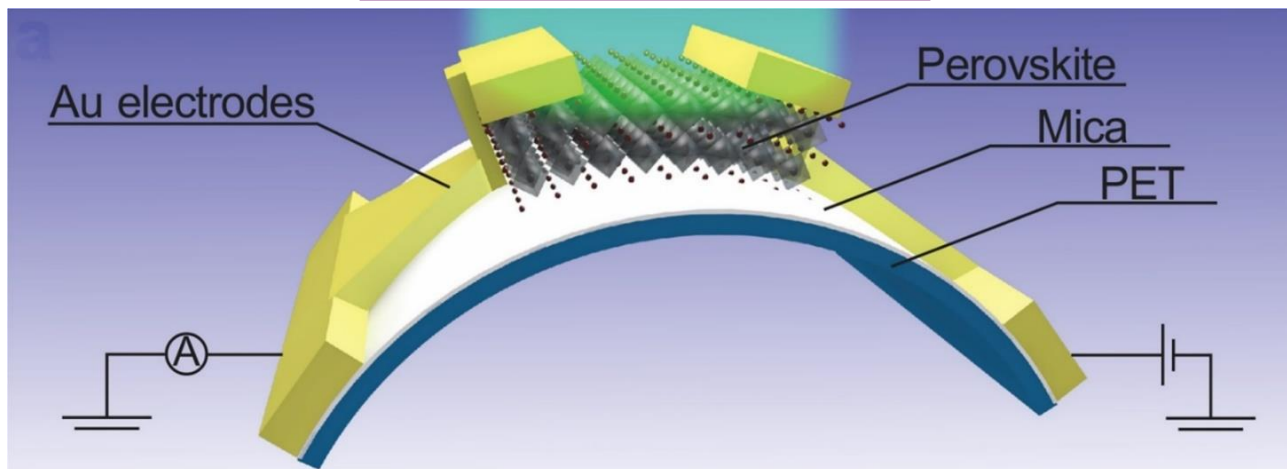
EDS能谱仪分析



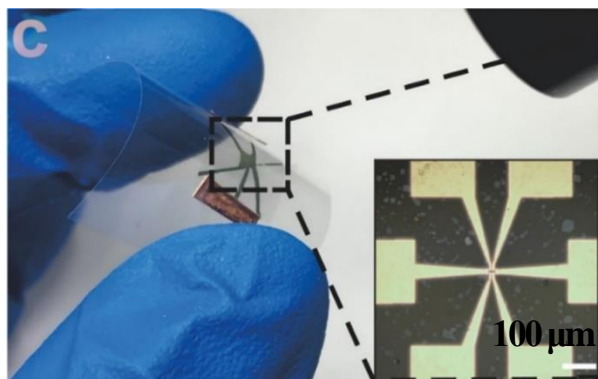
Hao Jing, Ruwen Peng*, Ren-Min Ma*, ... and Mu Wang*,
Nano Letters 20, 7144-7151 (2020)

钙钛矿柔性光电探测器

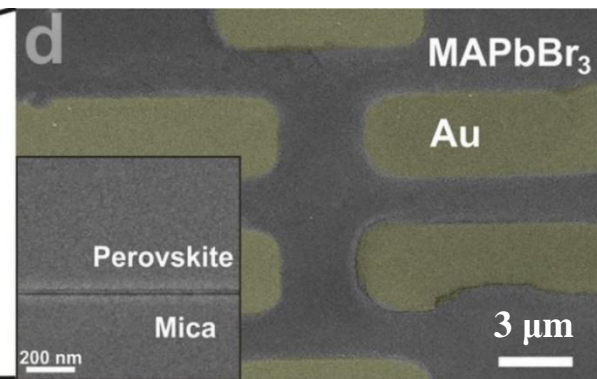
示意图



显微光学照片

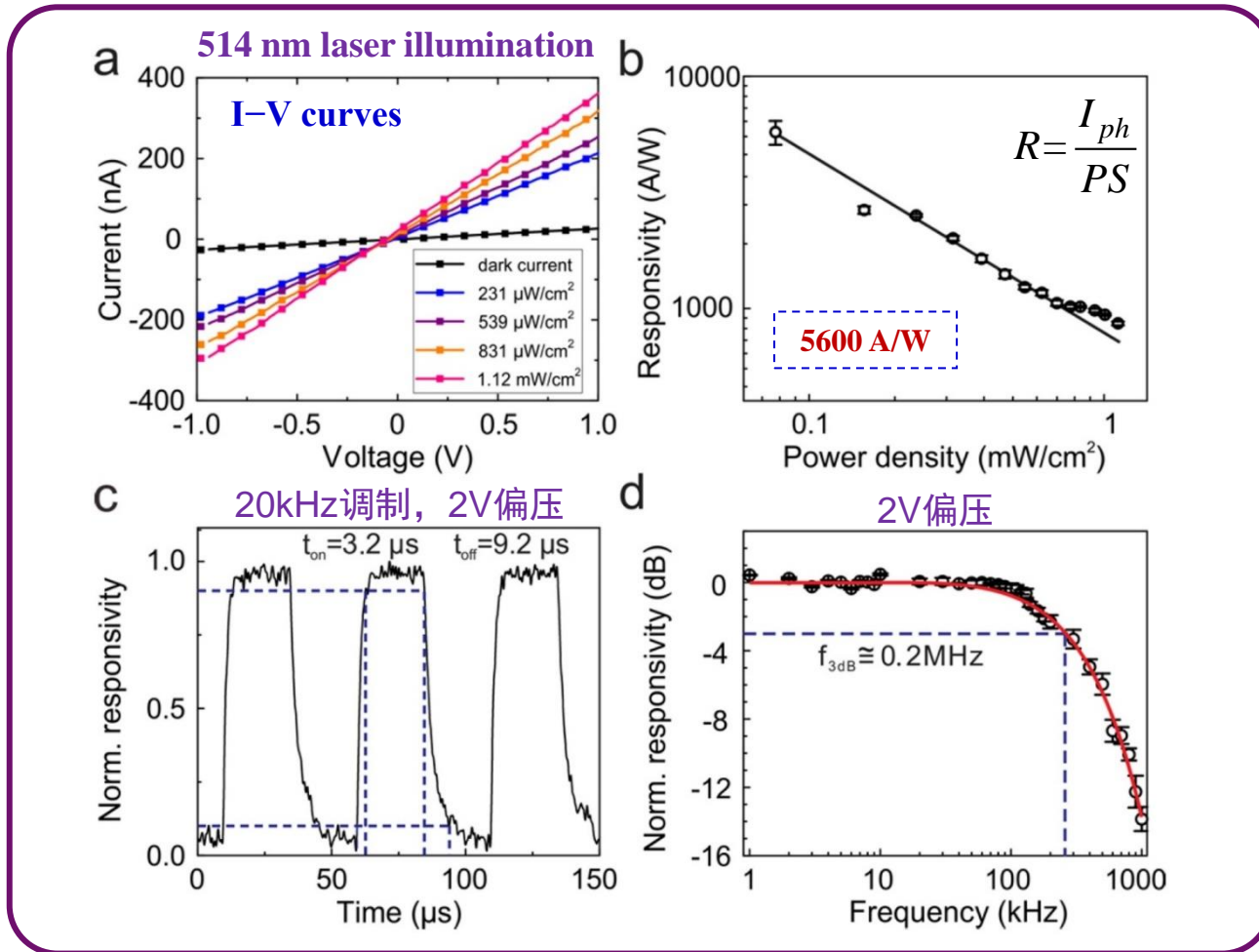


SEM 图像



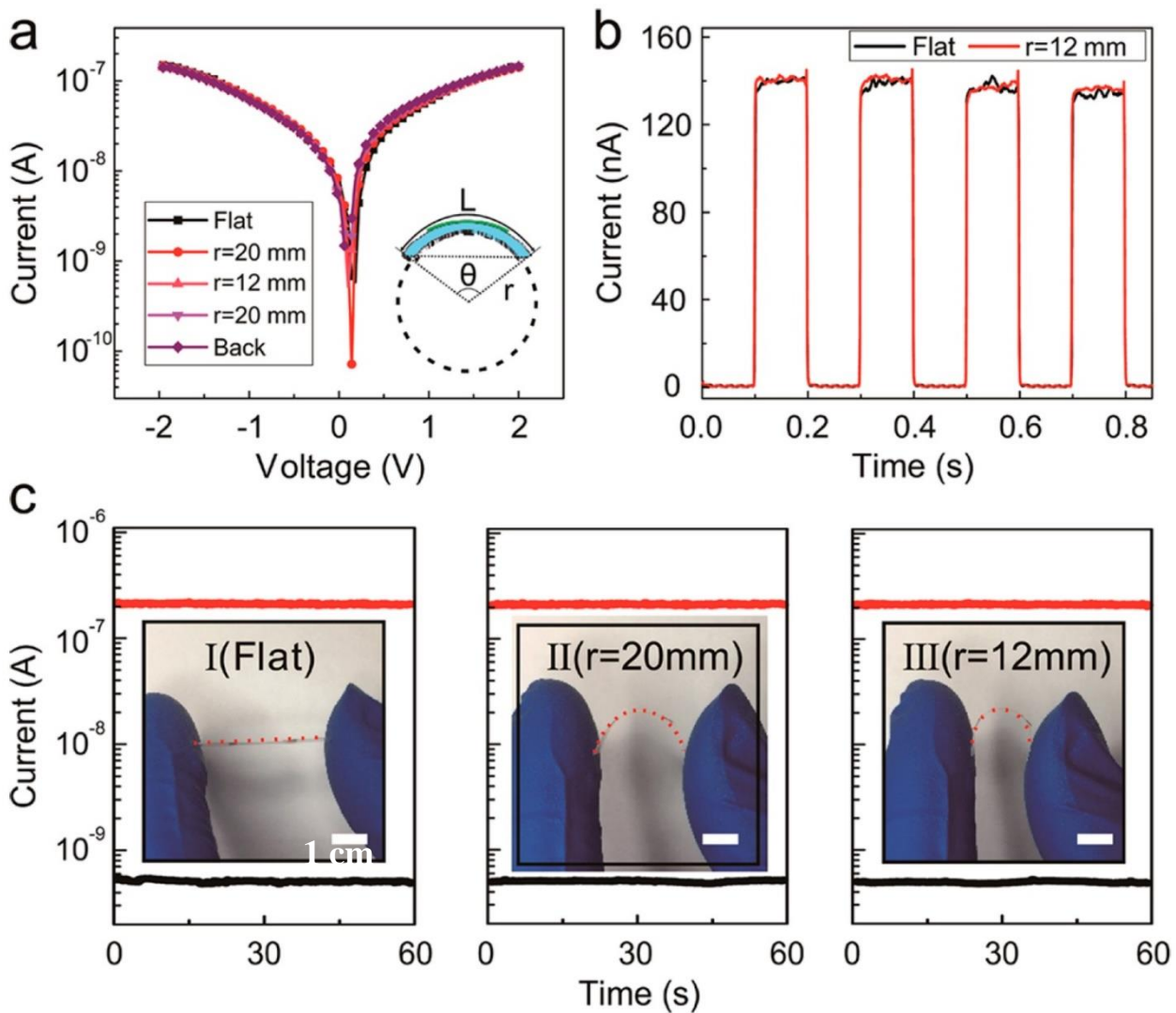
Hao Jing, Ruwen Peng*, Ren-Min Ma*, ... and Mu Wang*,
Nano Letters 20, 7144-7151 (2020)

柔性光电探测器的探测性能

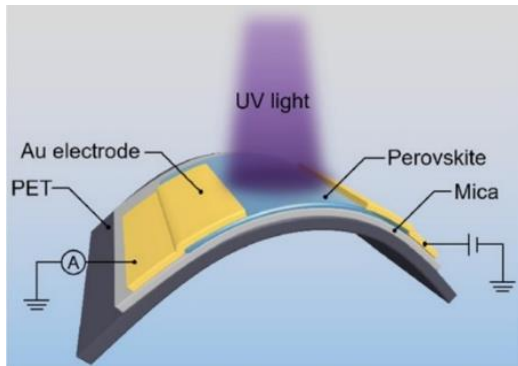


device structure	material structure	D^* [Jones]	responsivity [A/W]	rise/decay time [ms]	device area	on/off ratio
Au/MAPbBr ₃ /Au	ultrathin single crystal ~20 nm	6.59×10^{11}	5600@1 V@514 nm	0.003/0.009	$36 \mu\text{m}^2 \sim 100 \mu\text{m}^2$	200

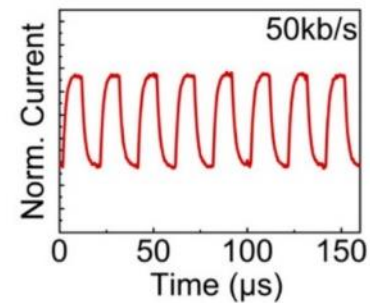
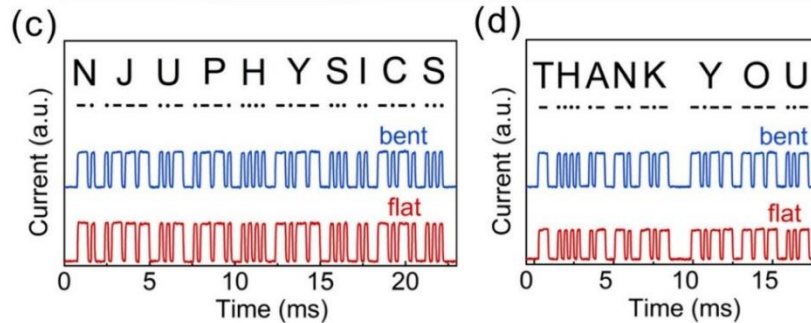
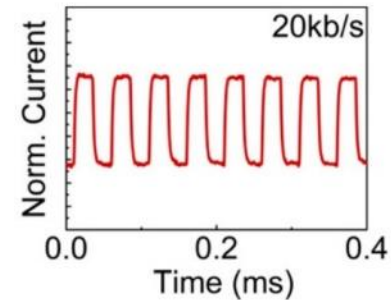
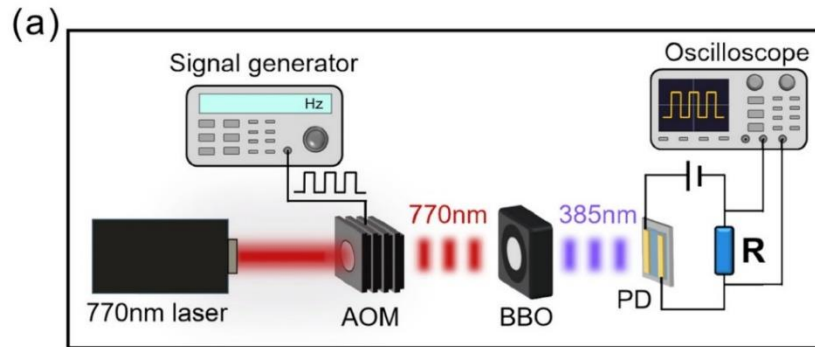
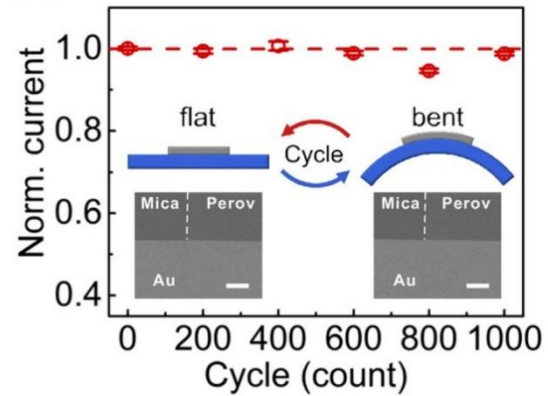
柔性光电探测器的弯曲稳定性



柔性光电探测器用于紫外光通讯



Responsivity:
24 A/W
@ 325 nm
@ 1V



C. Y. Li et al., Appl. Phys. Lett. 119, 251105 (2021)

1. 背景

2. 基于钙钛矿超构材料的光电探测器

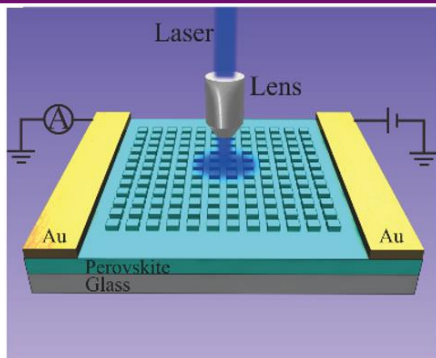
3. 钙钛矿柔性光电探测器

4. 总结



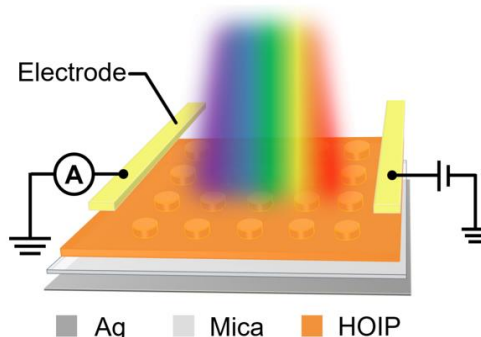
总结

Perovskite metamaterial for photon-to-electron conversion



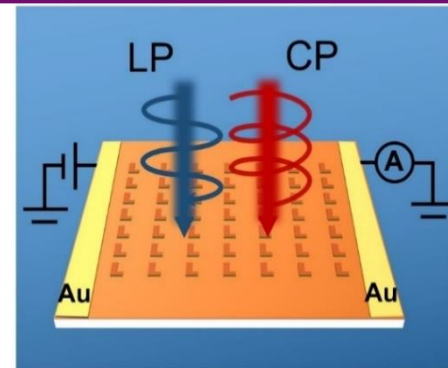
H. Jing et al., *Nanophotonics* 9, 3323-3333 (2020)

Improving photoelectric conversion with broadband perovskite metasurface



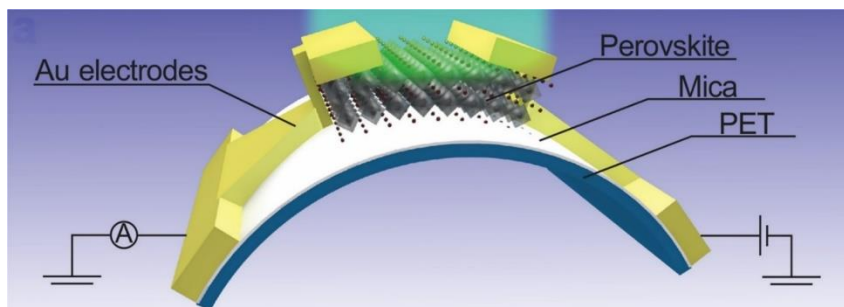
J. He et al., *Nano Letters* 22, 6655-6663 (2022)

Multiple-polarization-sensitive photodetector



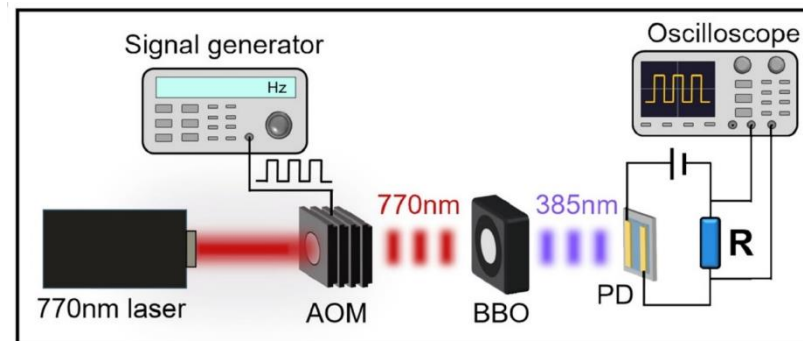
C. Y. Li et al., *Optics Letters* 47, 565 (2022)

Flexible ultrathin single-crystalline perovskite photodetector



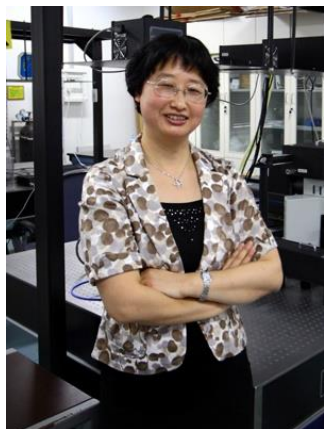
H. Jing et al., *Nano Letters* 20, 7144-7151 (2020)

Flexible perovskite photodetectors for UV communication



C. Y. Li et al., *Appl. Phys. Lett.* 119, 251105 (2021)

致谢



彭茹雯



王牧



祁冬祥



景灏



李成尧



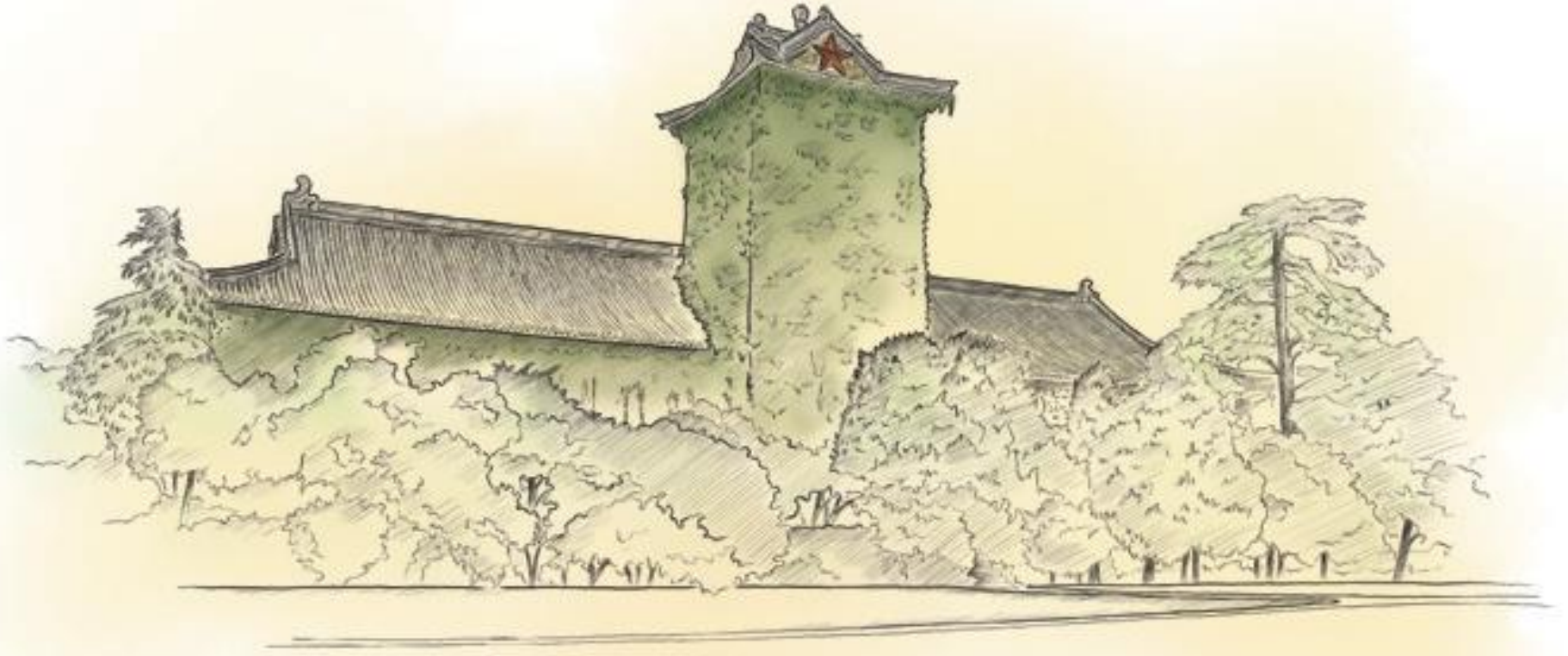
何捷



MOST of China



NSF of China



Thank you!