

Перовскитные светоизлучающие и лазирующие нано- и микроструктуры

Сергей Макаров

рук. Лаборатории Гибридной Нанофотоники и Оптоэлектроники
("PeroLab")

Университет ИТМО



Санкт-Петербург, Россия



ФТИ, 15.04.2019



- ✓ Introduction to halide perovskites
- ✓ Reversibly tunable perovskite nanoantennas
- ✓ Extremely fast method of nanowire lasers synthesis
- ✓ Large-scale laser printing of perovskite microlasers
- ✓ All-dielectric nanolasers...



I. Introduction to perovskites



Discovered perovskite...



Gustav Rose (1839)

sponsored...



Lev Perovski



CaTiO_3

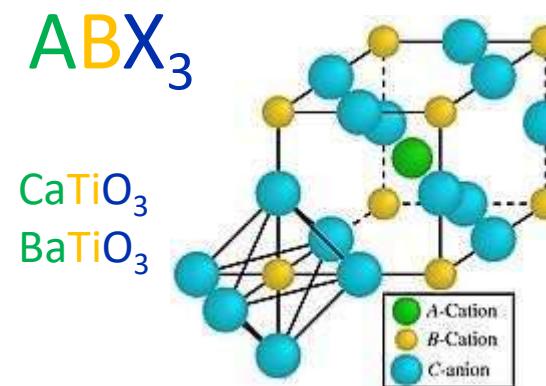
first perovskite (CaTiO_3) was discovered by **Gustav Rose** in 1839 in Ural mountains of Russia and named after Russian minister and mineralogist **Lev Perovski**.



Described
perovskite structure



Victor Goldschmidt (1938)



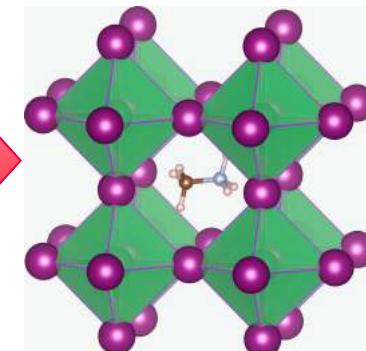
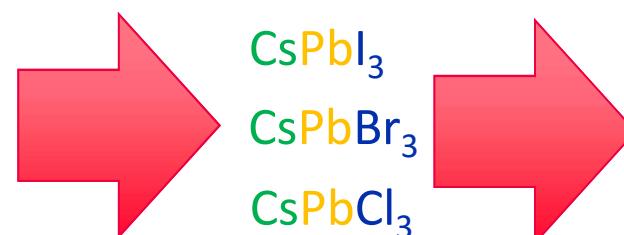
Halide perovskites

- J. Phys. C12 (1979) 5933.
- J. Phys. Soc. Jpn. 47 (1979) 232.
- Acta Cryst. A36 (1980) 7.

First organic-inorganic
halide perovskites



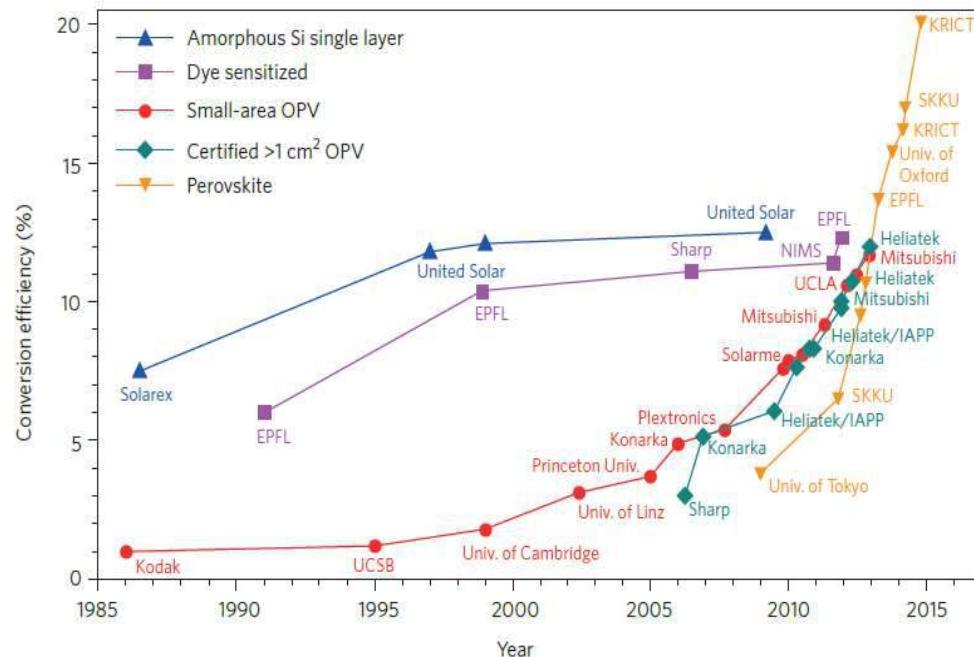
David Mitzi @ IBM
(around 1995)



MAPbI_3
 MAPbBr_3
 MAPbCl_3
MA = CH_3NH_3

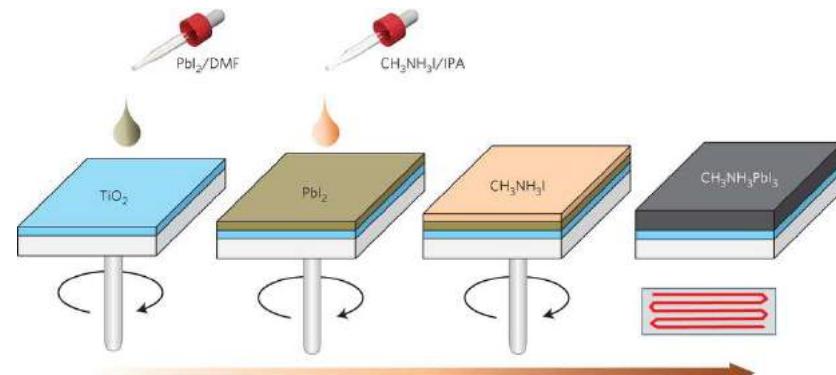


Thin film photovoltaics



23.3% (2018)

wet chemistry processing



✓ Low cost process

✓ Flexible substrate

✓ Tandem Perovskite-Silicon application



ARTICLE

Received 19 Aug 2016 | Accepted 20 Apr 2017 | Published 1 Jun 2017

DOI: 10.1038/ncomms15684

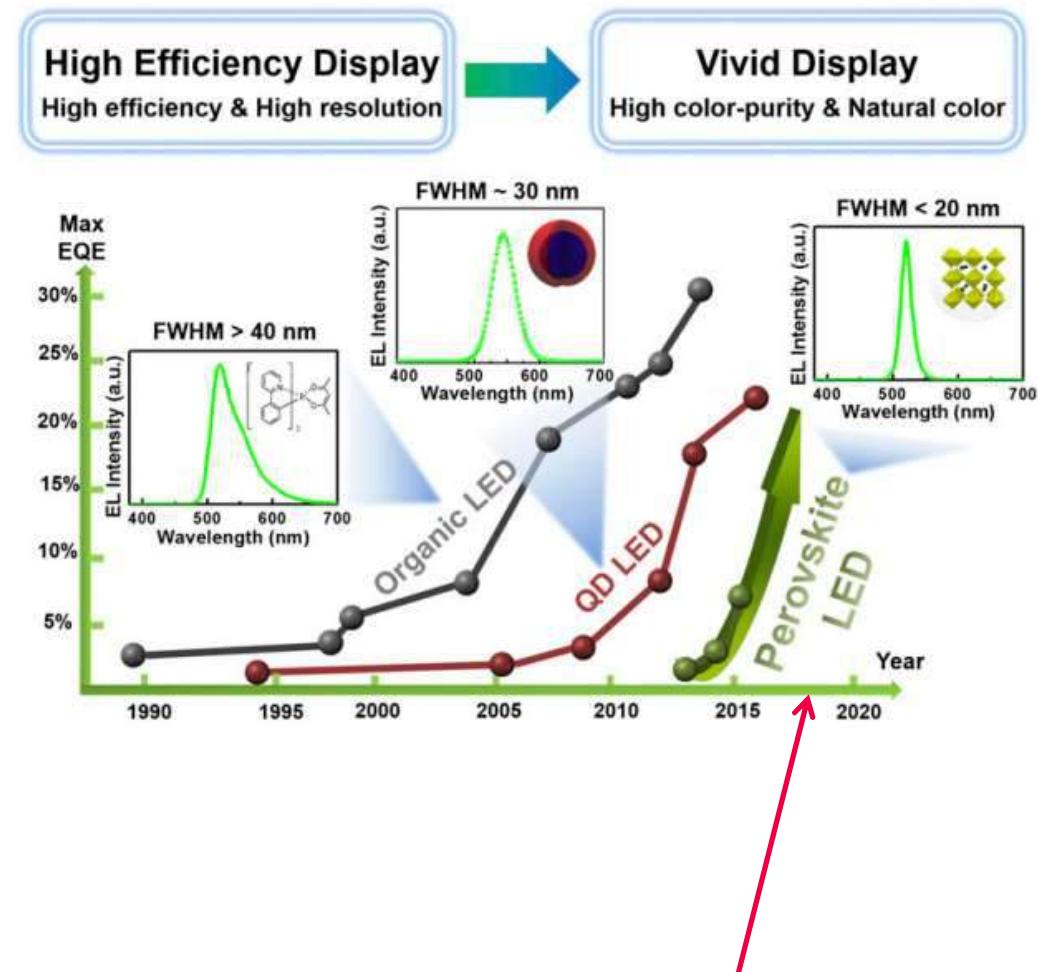
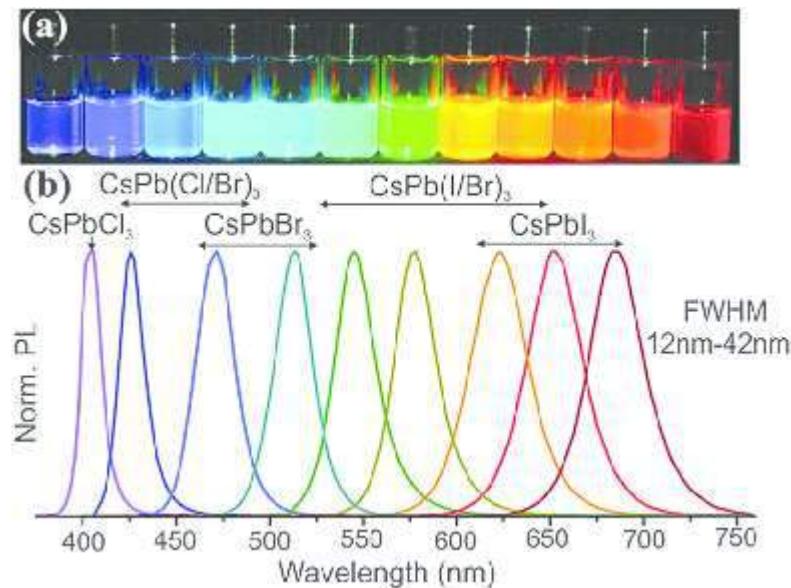
OPEN

One-Year stable perovskite solar cells by 2D/3D interface engineering

G. Grancini¹, C. Roldán-Carmona¹, I. Zimmermann¹, E. Mosconi^{2,3}, X. Lee⁴, D. Martineau⁵, S. Narbey⁵, F. Oswald⁵, F. De Angelis^{2,3}, M. Graetzel⁴ & Mohammad Khaja Nazeeruddin¹



Bulk perovskites and quantum dots

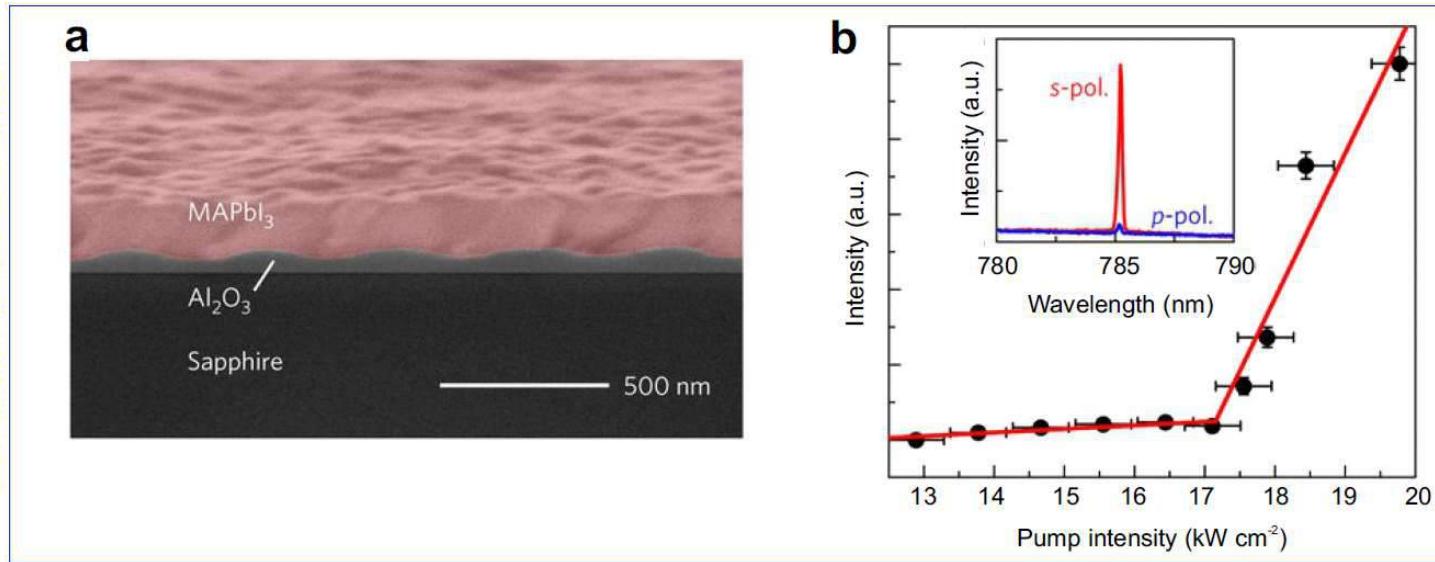


- ✓ High PL quantum yield: 50-90%
- ✓ Tuning in entire visible range
- ✓ Narrow luminescence spectra
- ✓ Flexible

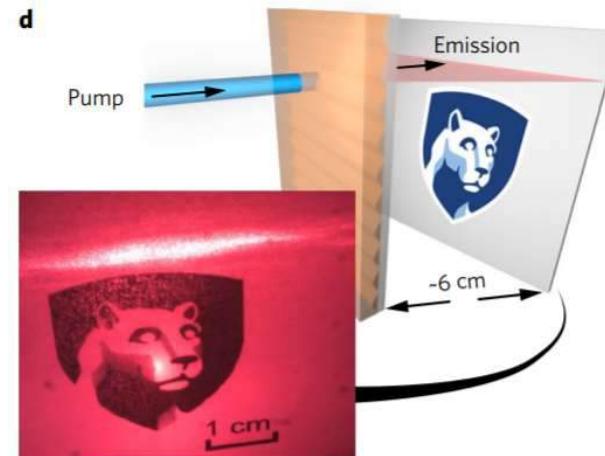
More than 20%
Nature 562 (7726), 245 (2018)

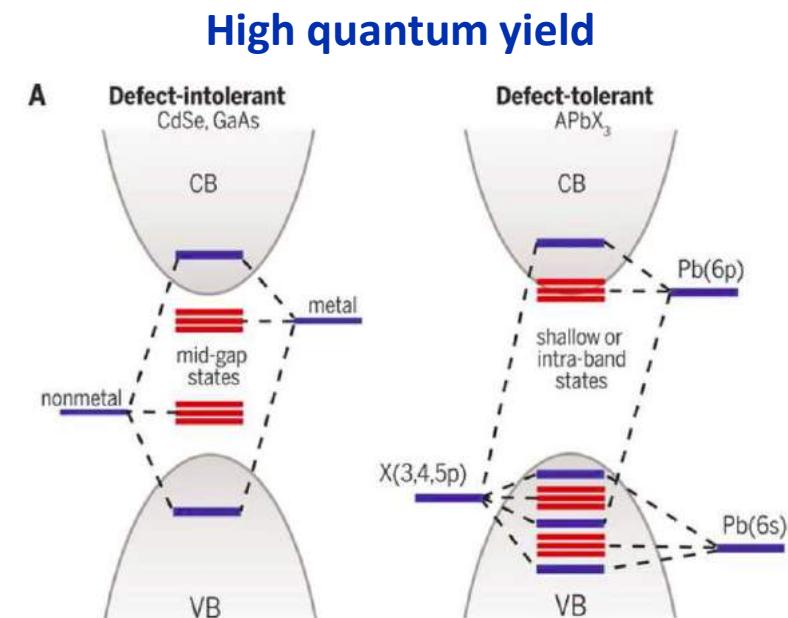
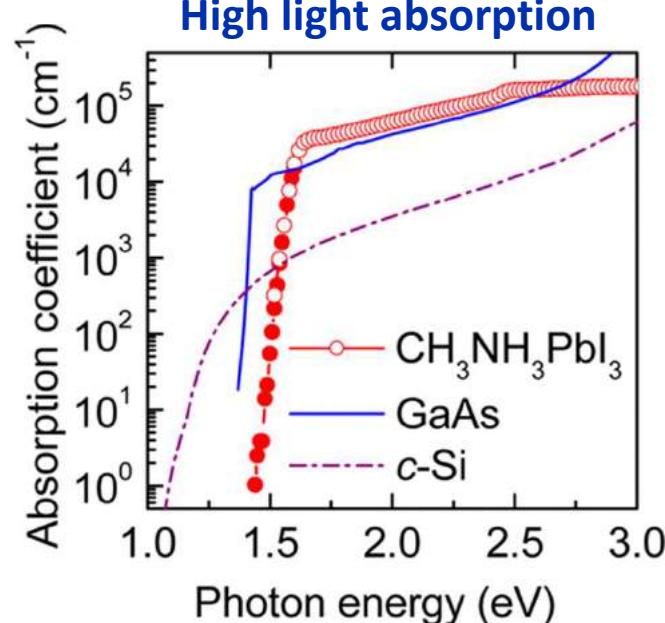
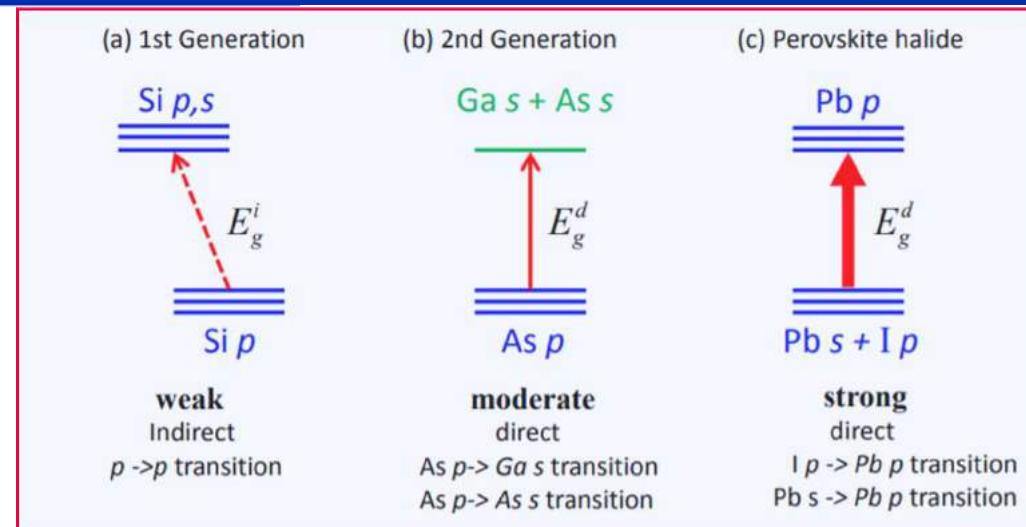


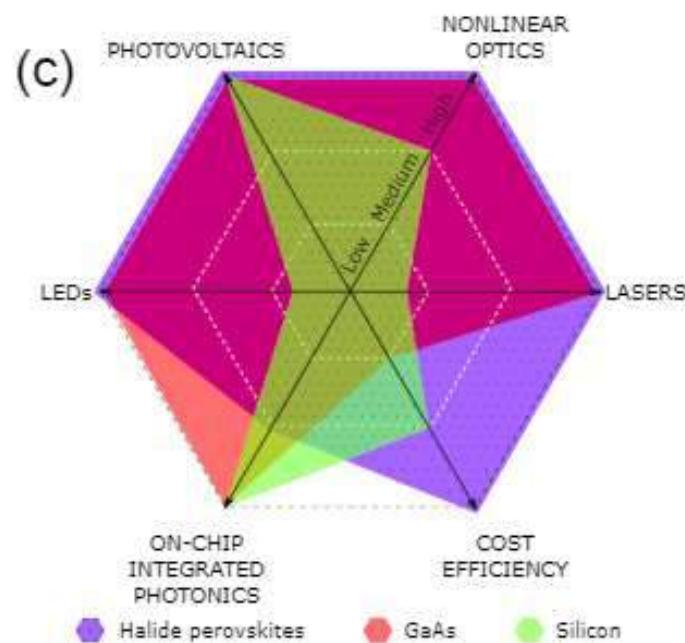
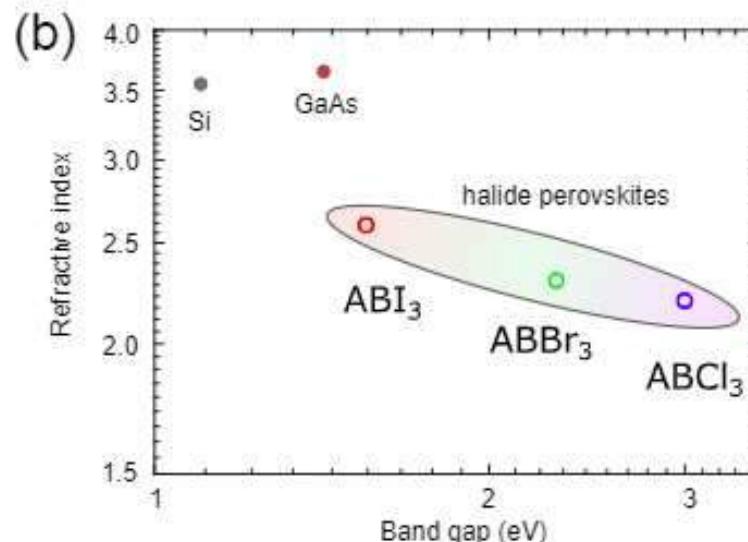
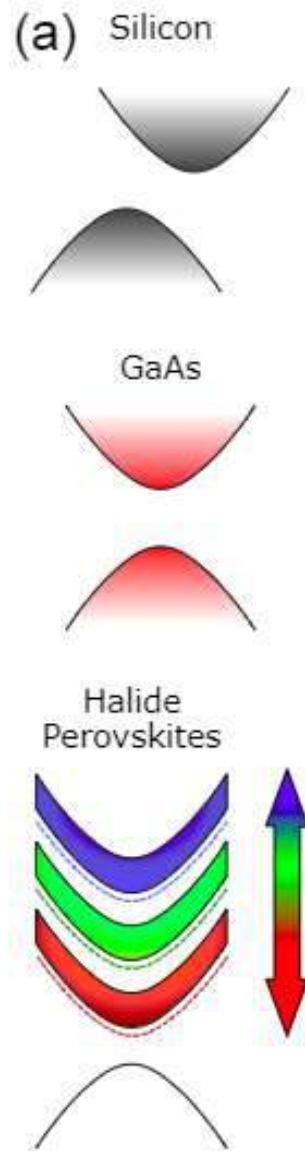
continuous wave excitation



- ✓ High gain, low-threshold
- ✓ Tuning in entire visible range
- ✓ Flexible
- ✓ Electrical pump is possible

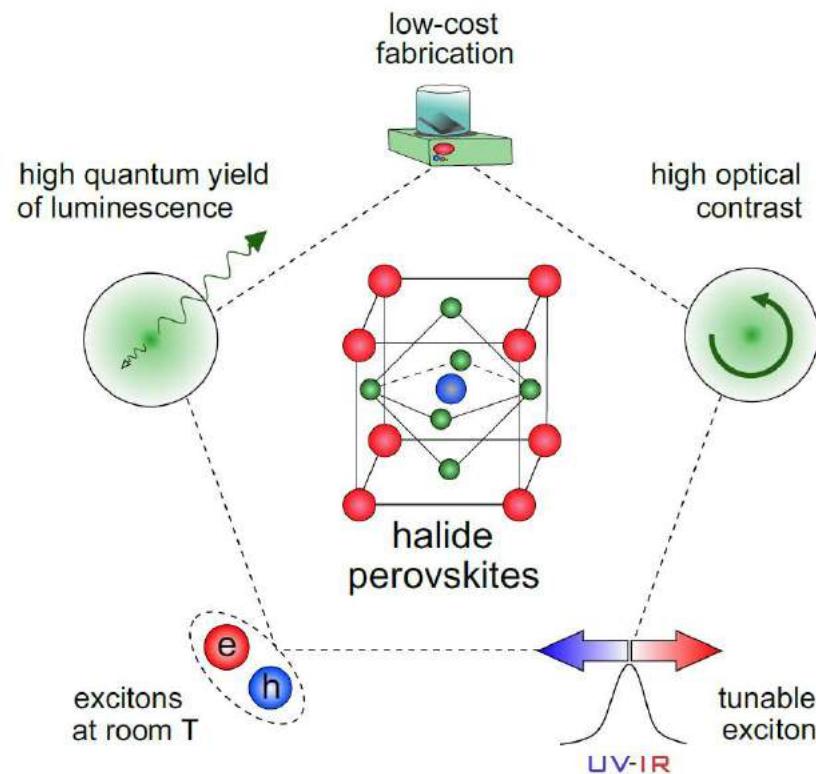




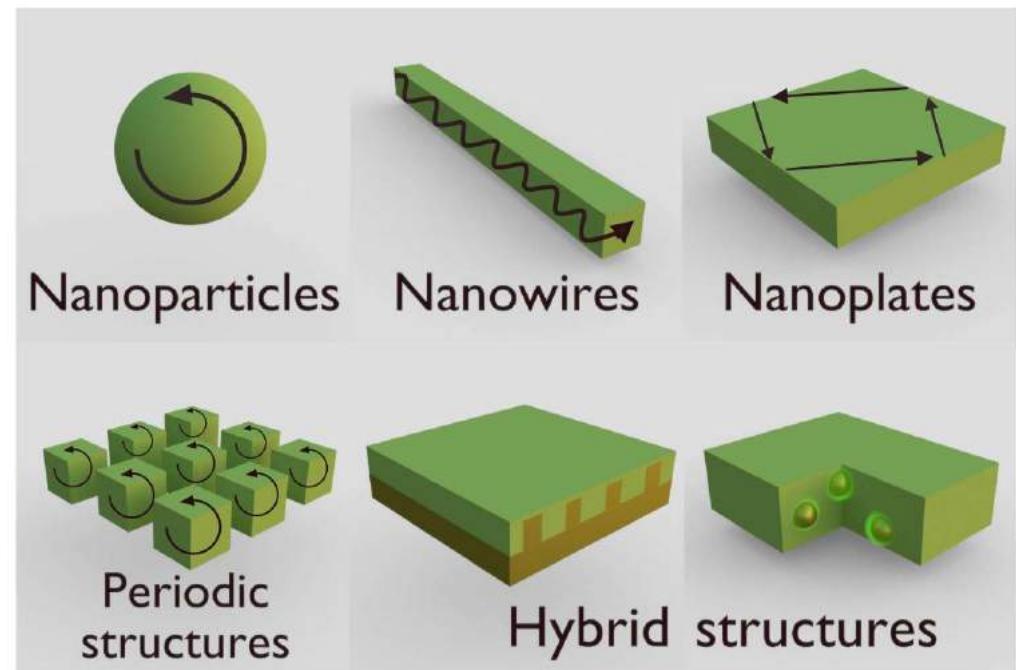




Why halide perovskites?



Basic designs



Makarov et al, "Halide-Perovskite Resonant Nanophotonics"
Advanced Optical Materials, 7 (1), 1800784 (2019)



ITMO UNIVERSITY

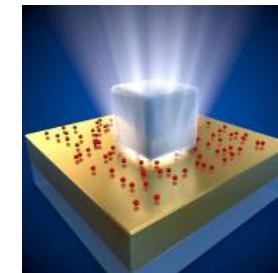
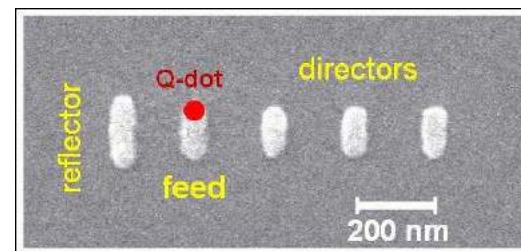
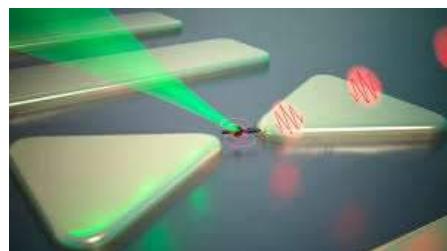
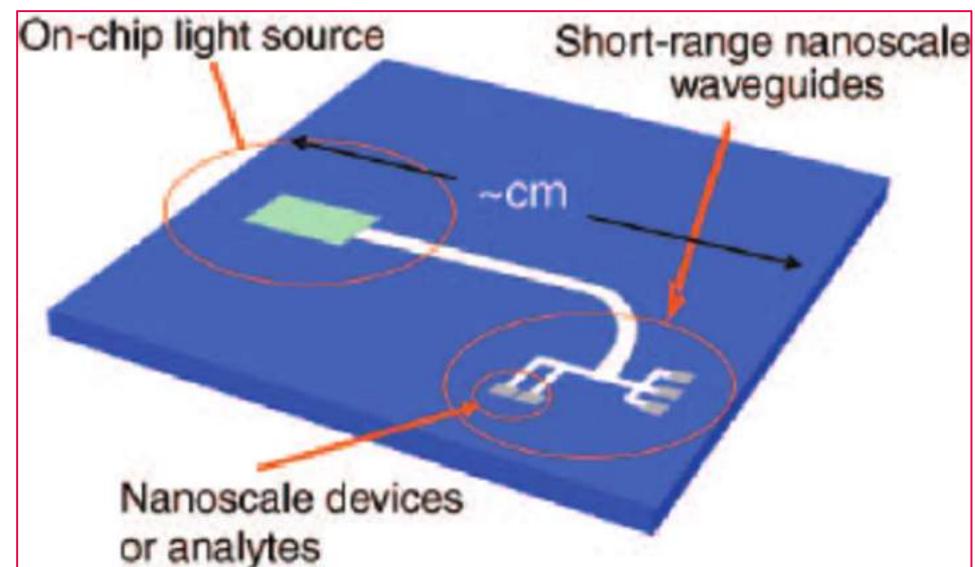
metalab.ifmo.ru

II. Perovskite based nanoscale light sources



Ultracompact photonic devices:

- optical modulators
- quantum computing
- gas sensors
- liquid sensors



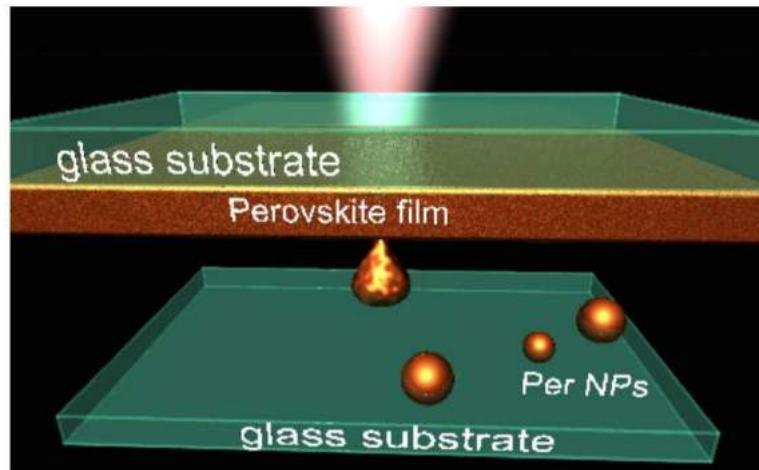


Problems of nanoscale light sources:

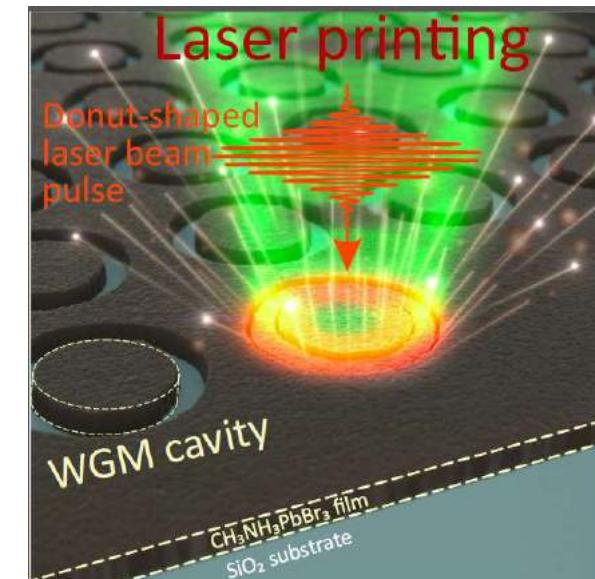
- ✓ Needs multistep and expensive lithography or epitaxial growth
- ✓ Difficult to tune spectrally
- ✓ Low quantum efficiencies of luminescence
- ✓ Difficult to integrate light source and nanoantenna



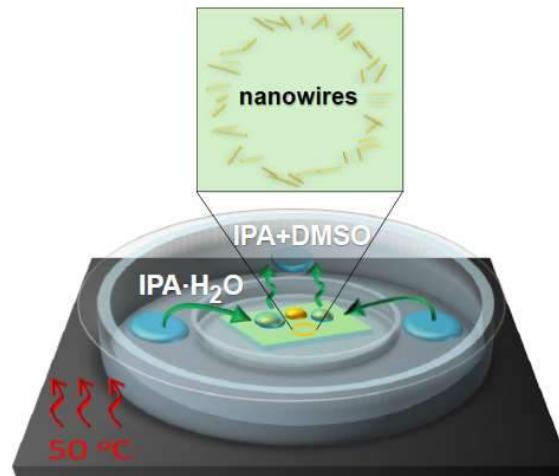
Laser transfer



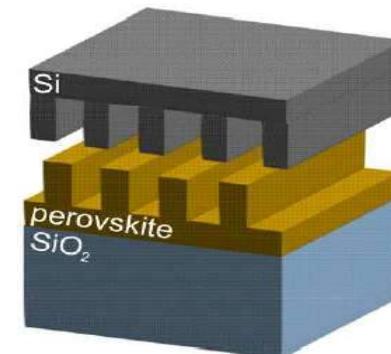
Direct laser imprinting



Chemically synthesized



Stamp-imprinted





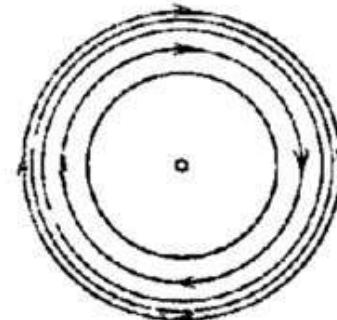
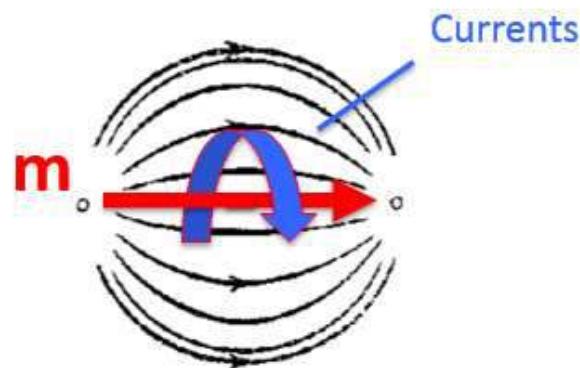
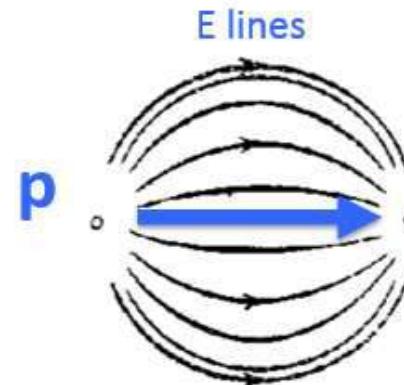
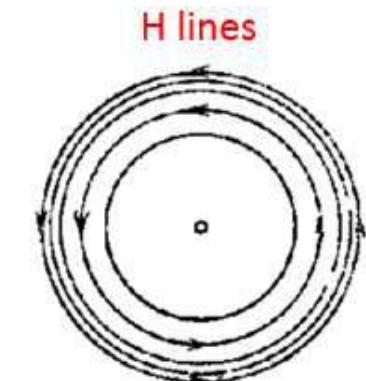
Nanoscale tunable light-sources





Gustav Mie

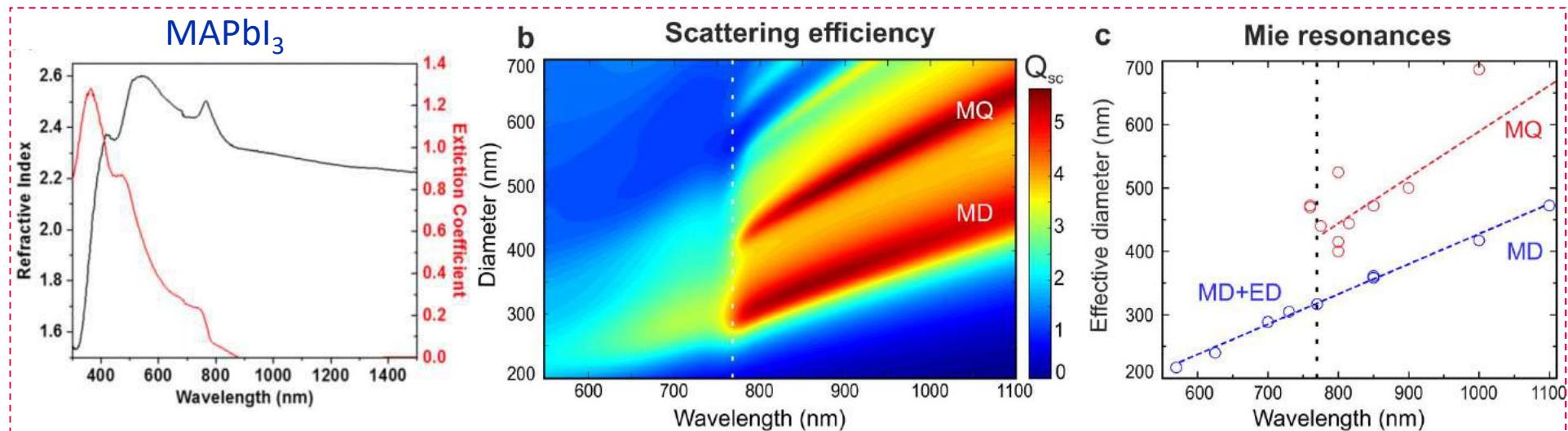
$$C_{\text{sca}} = \frac{W_{\text{sca}}}{I_i} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2)$$



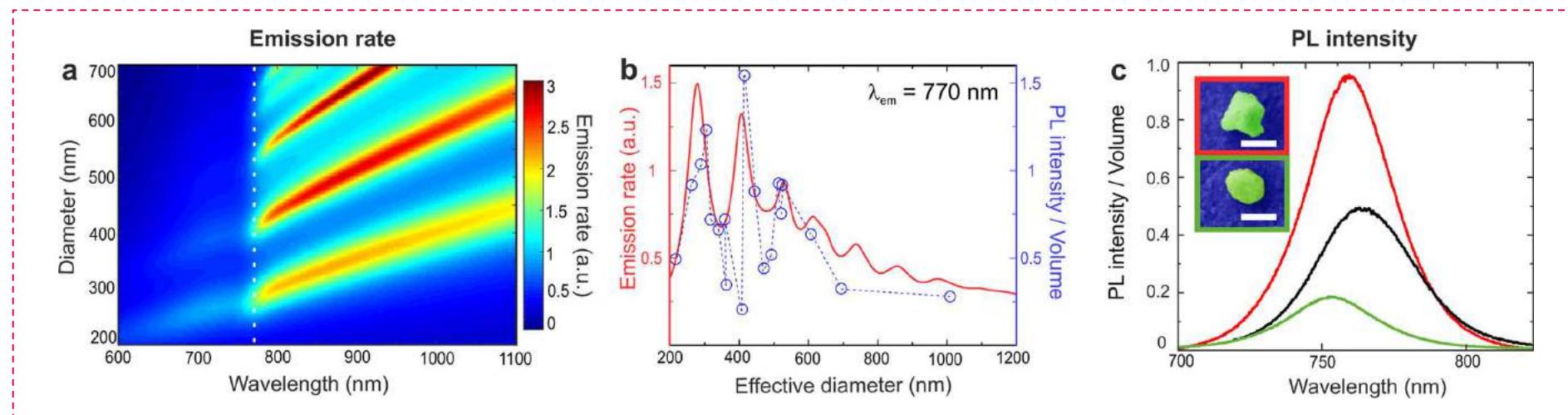
books Born&Wolf, Bohren&Huffman



Light scattering on perovskite NPs



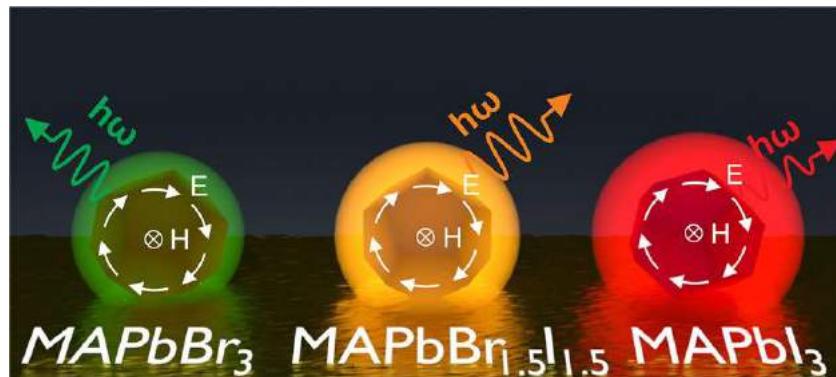
Emission rate enhancement



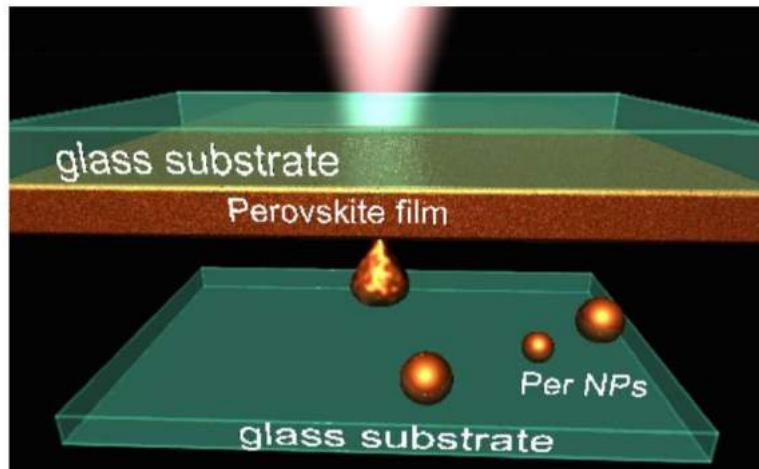


Perovskite resonant nanoparticles

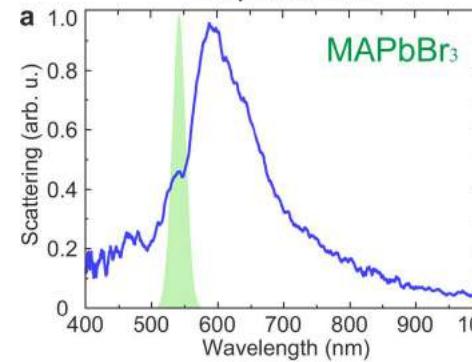
Color change



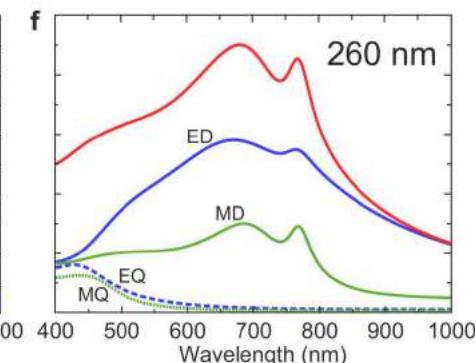
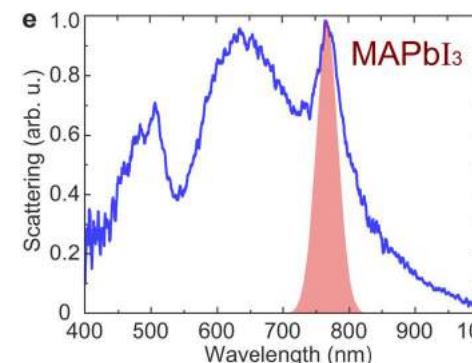
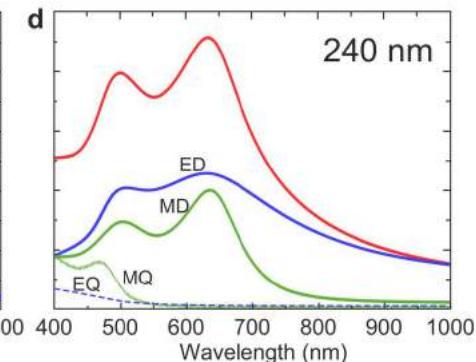
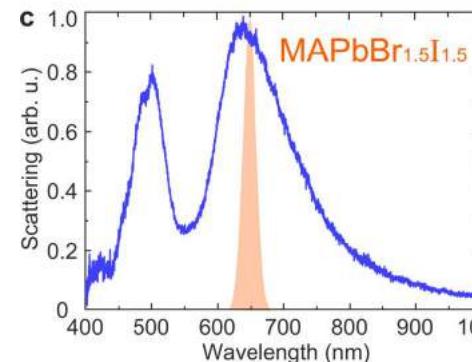
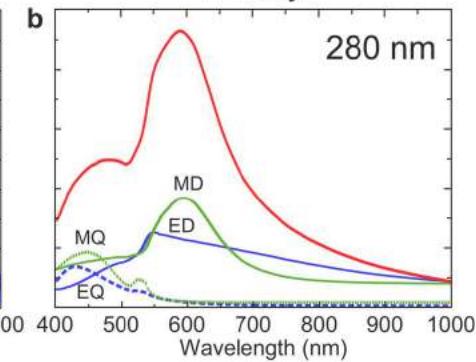
Laser printing



Experiment



Theory





Effects of Configuration Interaction on Intensities and Phase Shifts*

U. FANO

National Bureau of Standards, Washington, D. C.

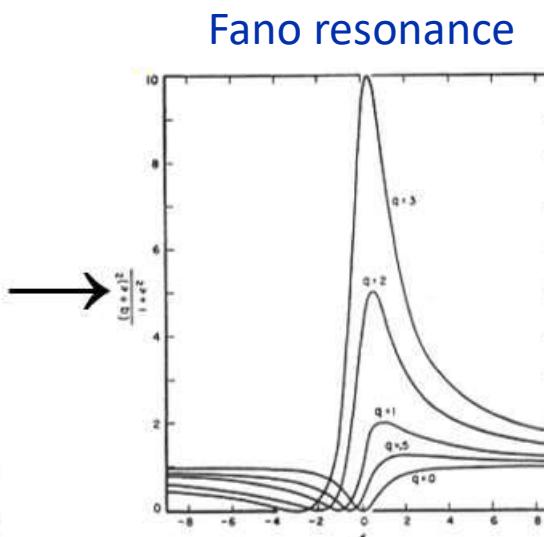
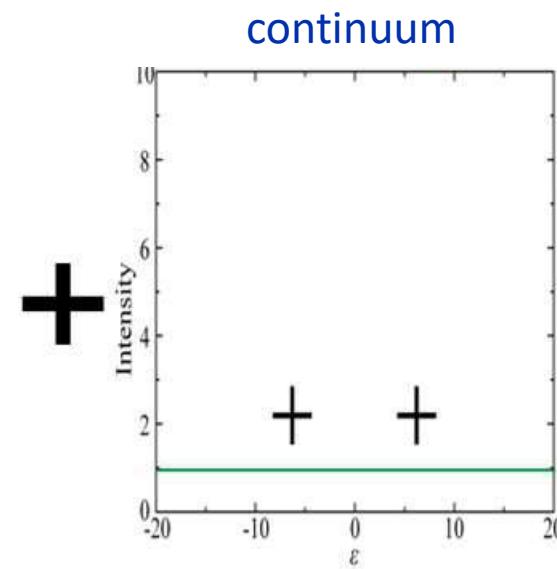
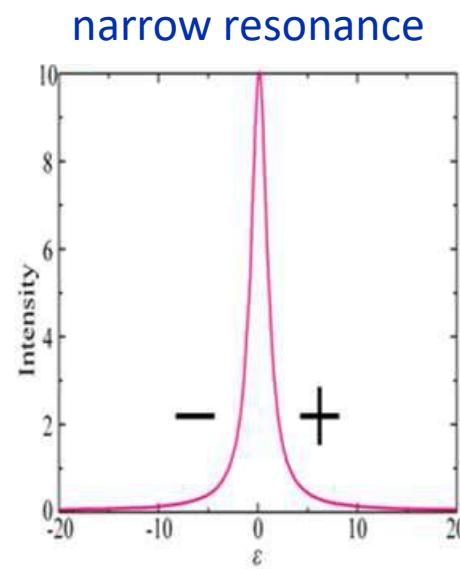
(Received July 14, 1961)

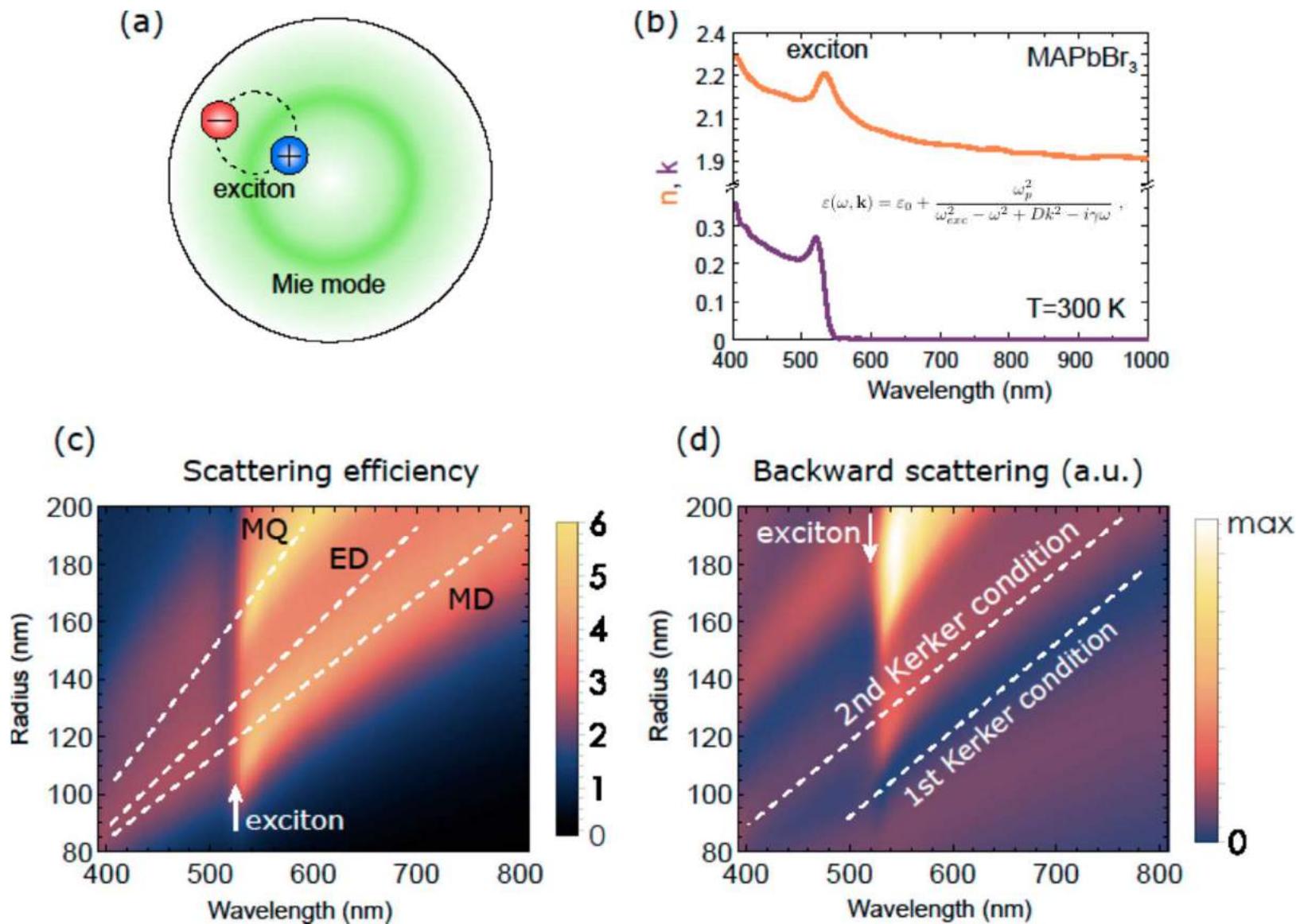
of phase normalizations. These curves are represented by

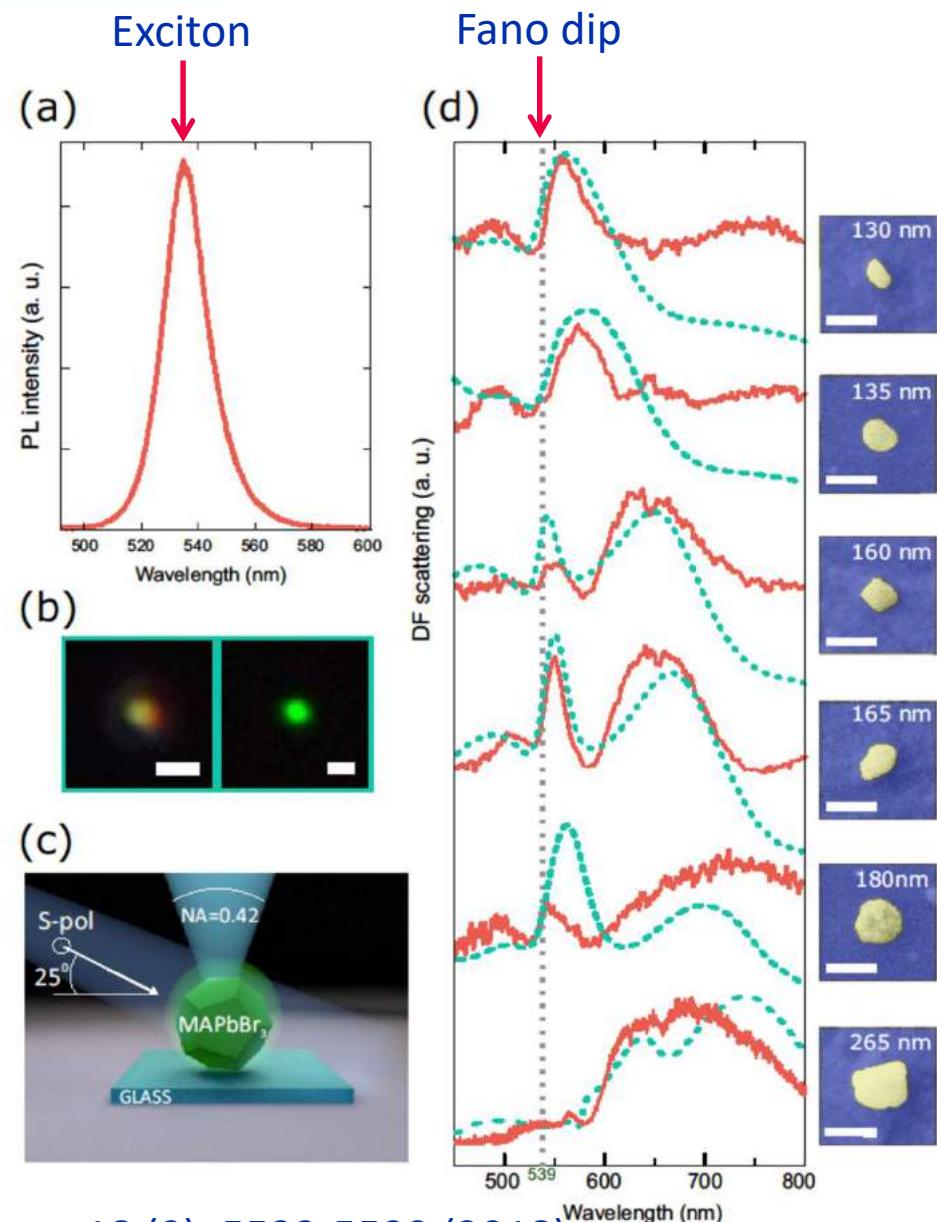
$$\frac{|\langle \Psi_E | T | i \rangle|^2}{|\langle \Psi_E | T | i \rangle|^2} = \frac{(q+\epsilon)^2}{1+\epsilon^2} = 1 + \frac{q^2 - 1 + 2q\epsilon}{1+\epsilon^2}. \quad (21)$$

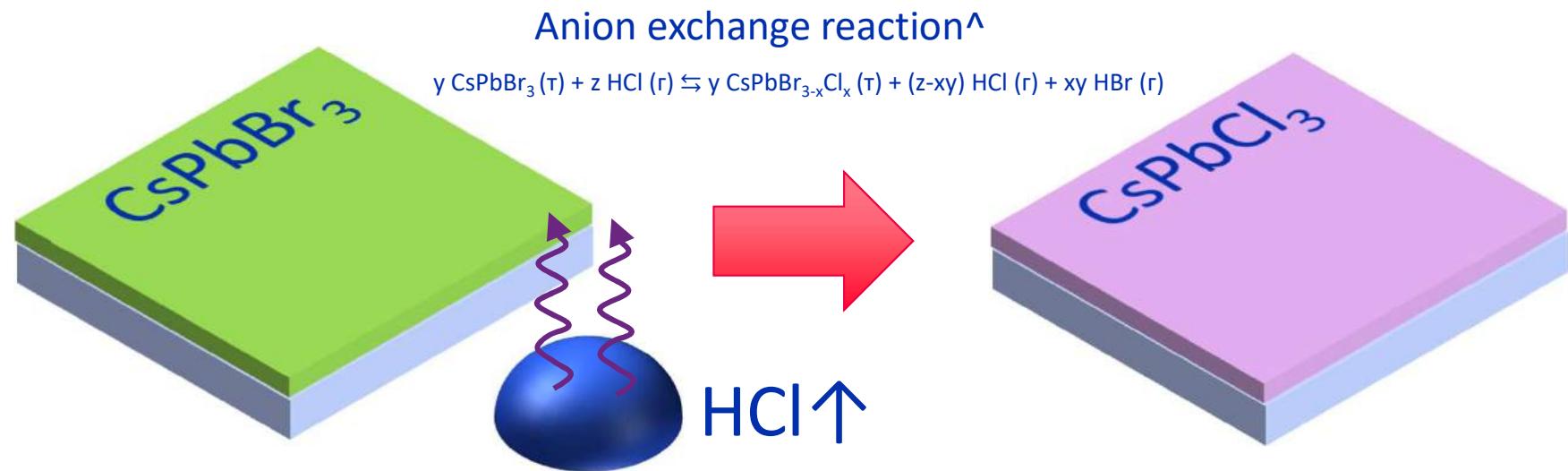
This function is plotted in Fig. 1 for a number of values of q , which is regarded as constant in the range of interest. Notice that

$$\frac{(q + \epsilon)^2}{1 + \epsilon^2}$$

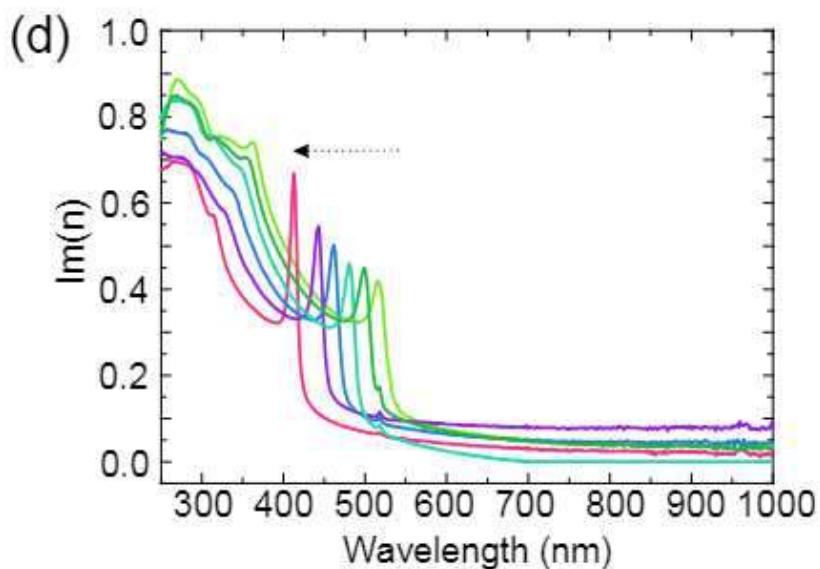
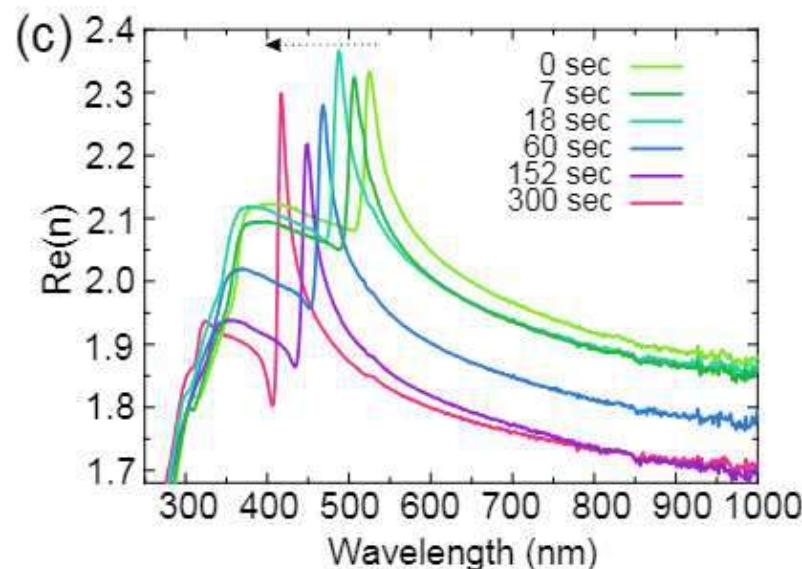
FIG. 1. Natural line shapes for different values of q . (Reverse the scale of abscissas for negative q .)

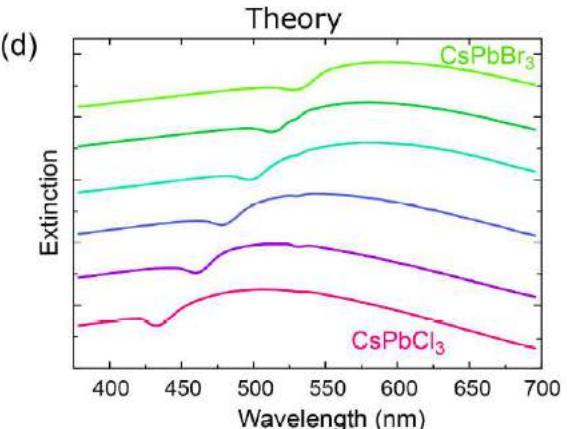
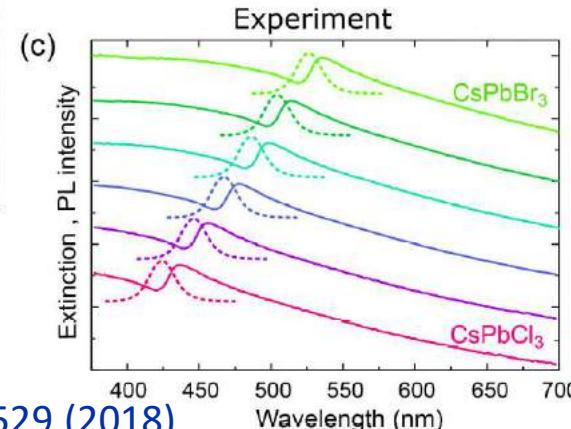
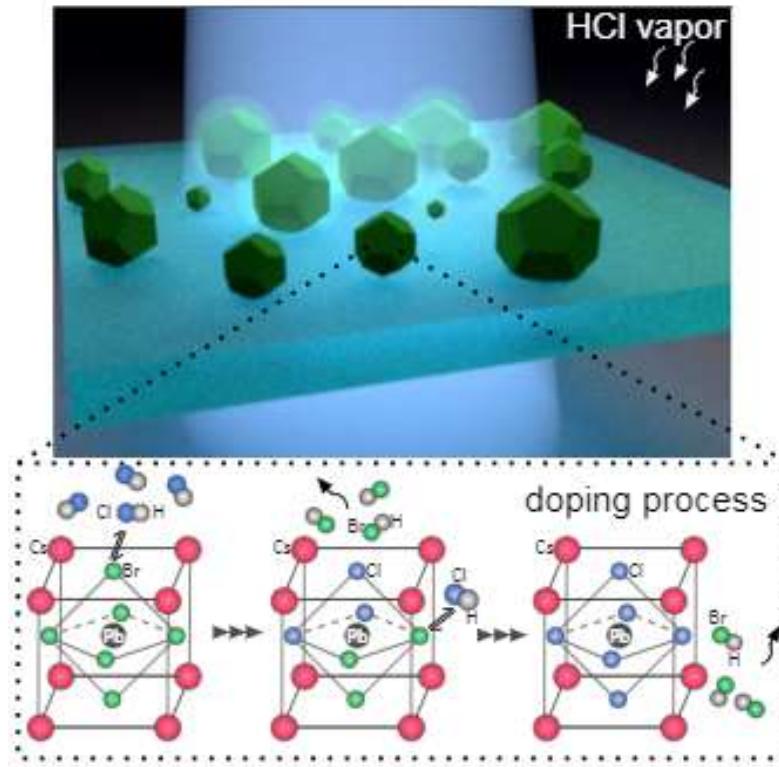
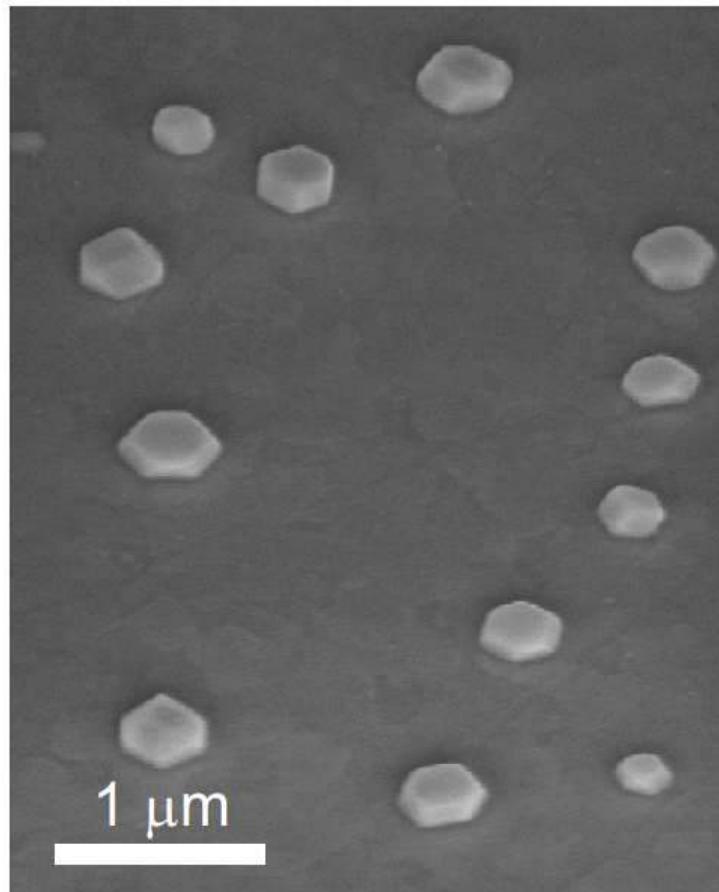


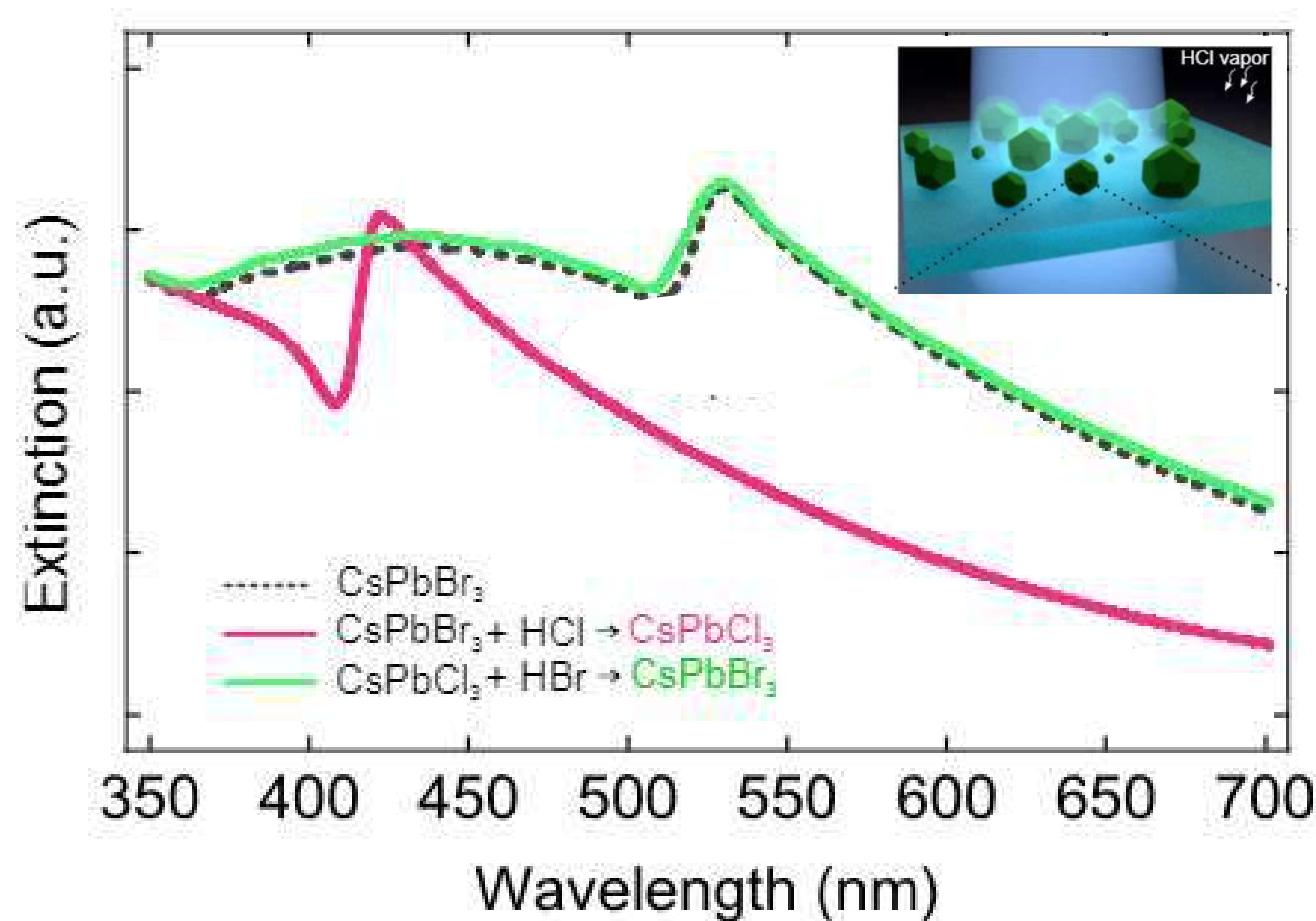
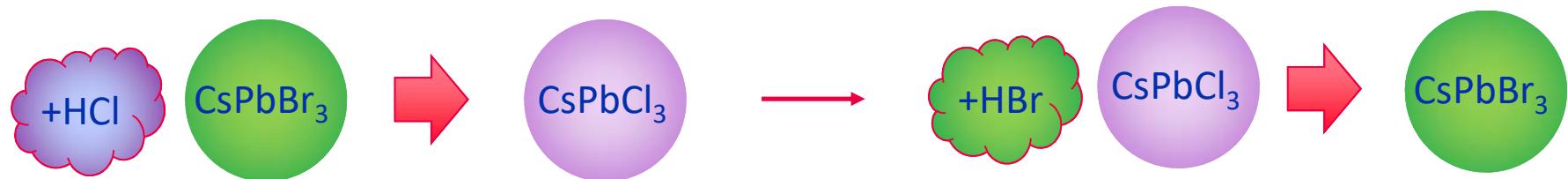


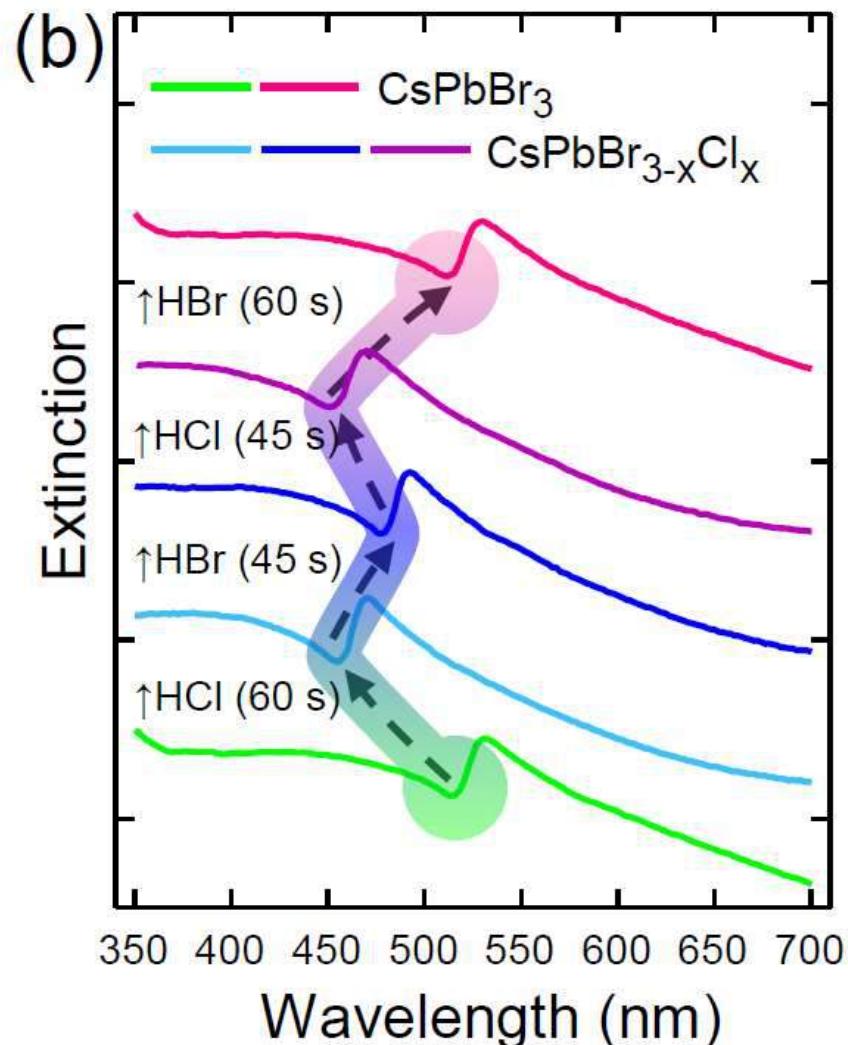
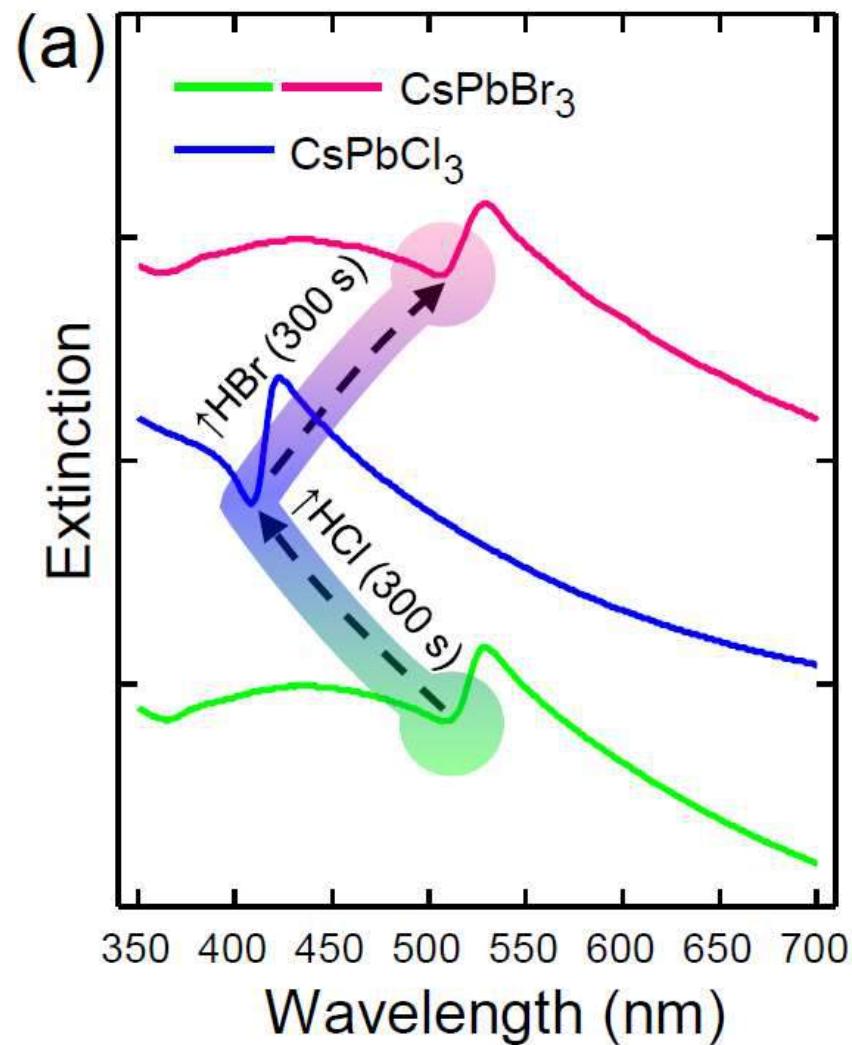


Ellipsometry data











$$\{D_x, D_y, D_z\} < \lambda$$

$$\{D_x, D_z\} < \lambda$$

$$D_z < \lambda$$



Mie resonances

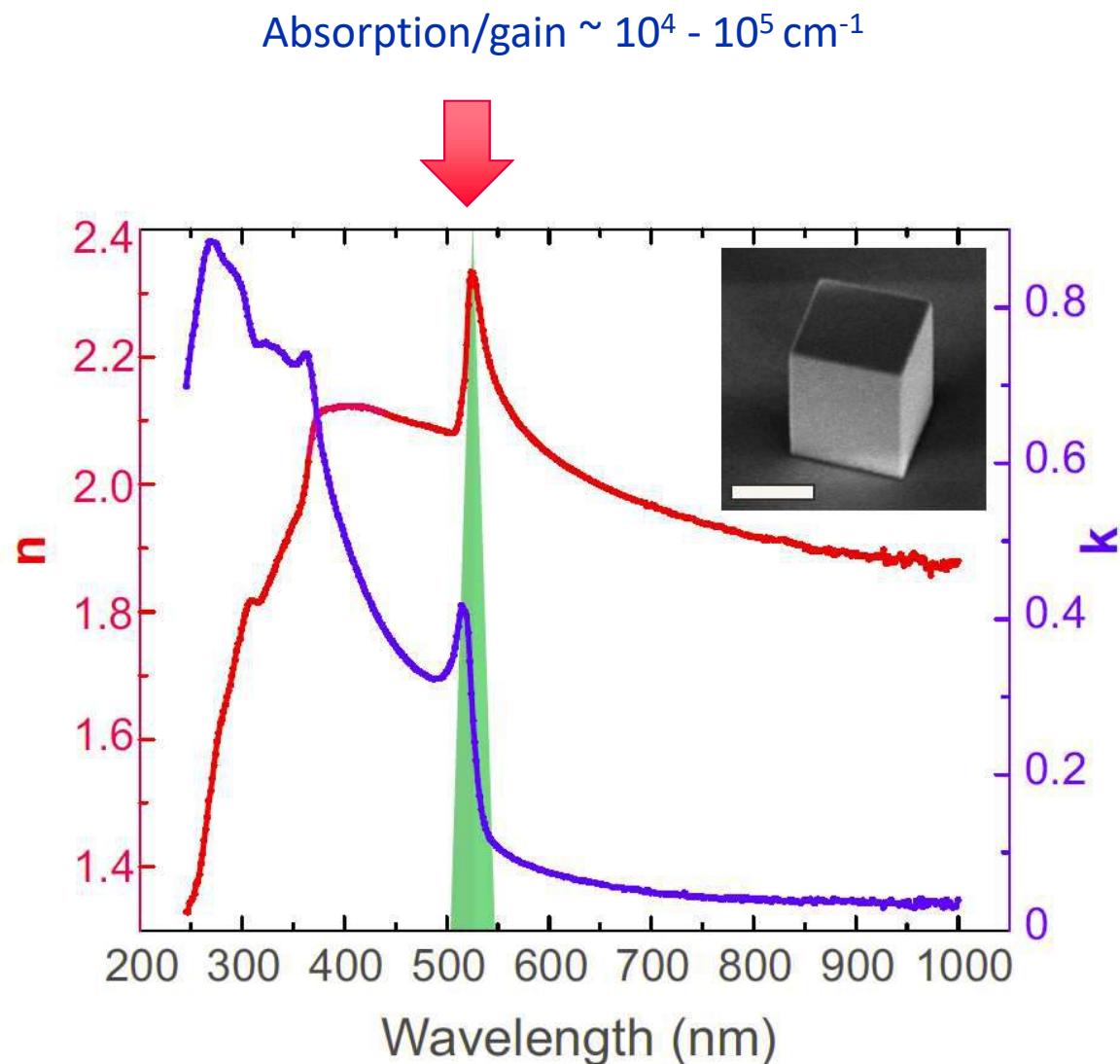
Fabry-Perot
resonances

Whispering
Gallery
modes





- ✓ High gain
- ✓ Easy to fabricate
- ✓ High quality
- ✓ Tunability



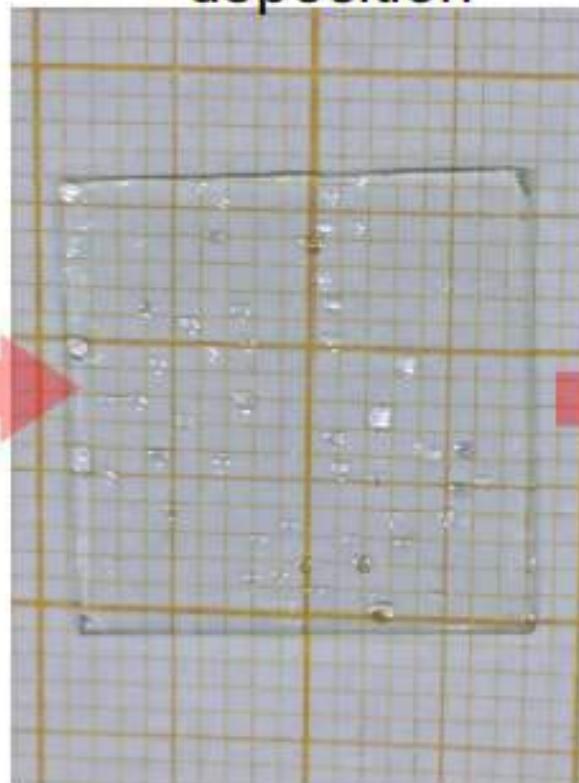


Few-minutes chemical synthesis

spraying



deposition

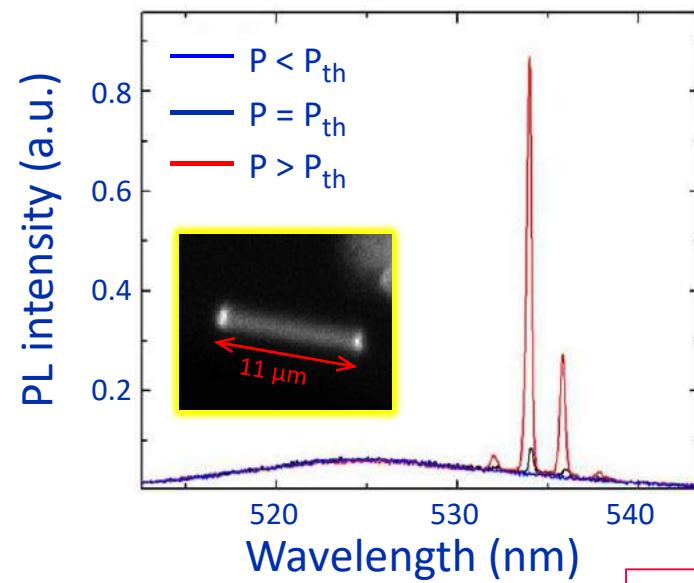
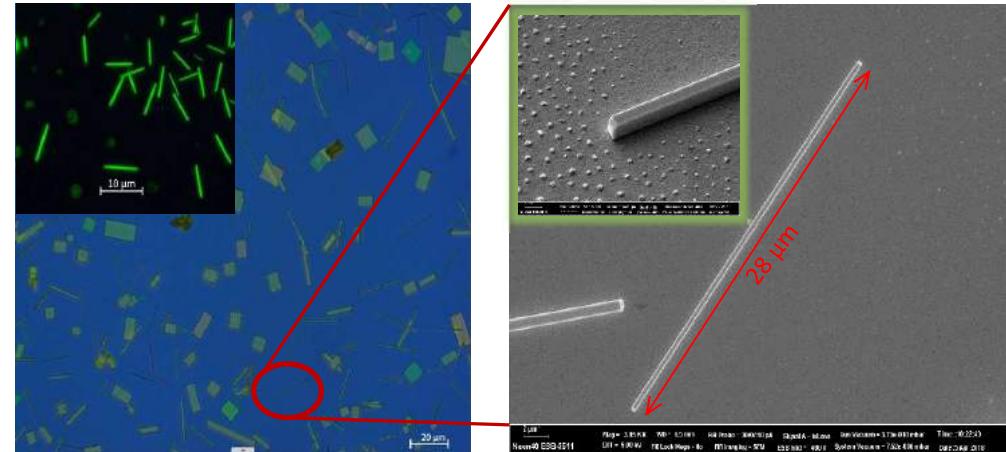
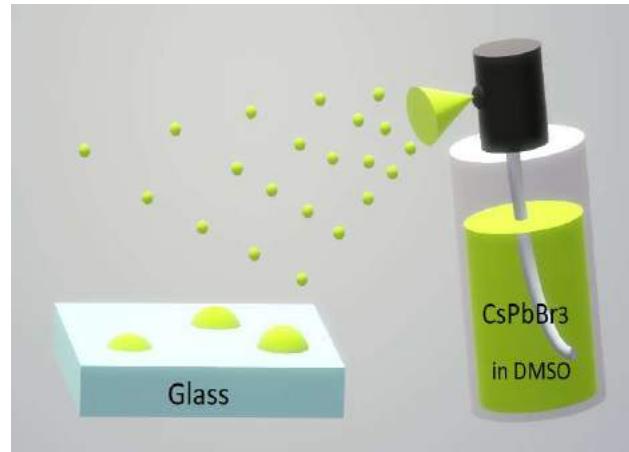


precipitation



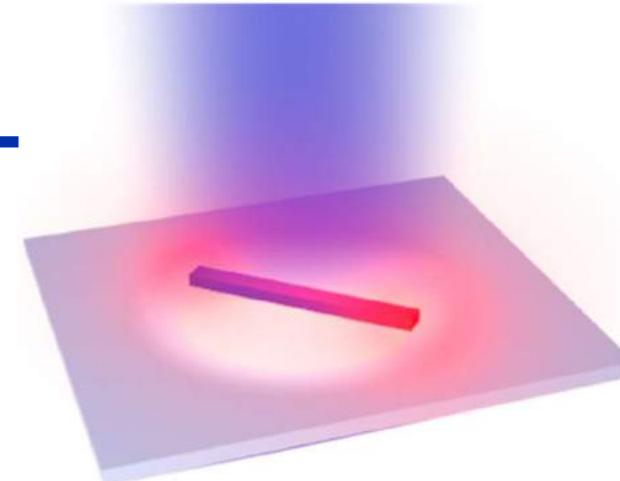


Lasing properties



$\lambda_{\max} = 534 \text{ nm}$
 $\delta\lambda = 0.25 \text{ nm}$
 $Q = 2100$
 $F_{\text{th}} \sim 50 \text{ uJ/cm}^2$

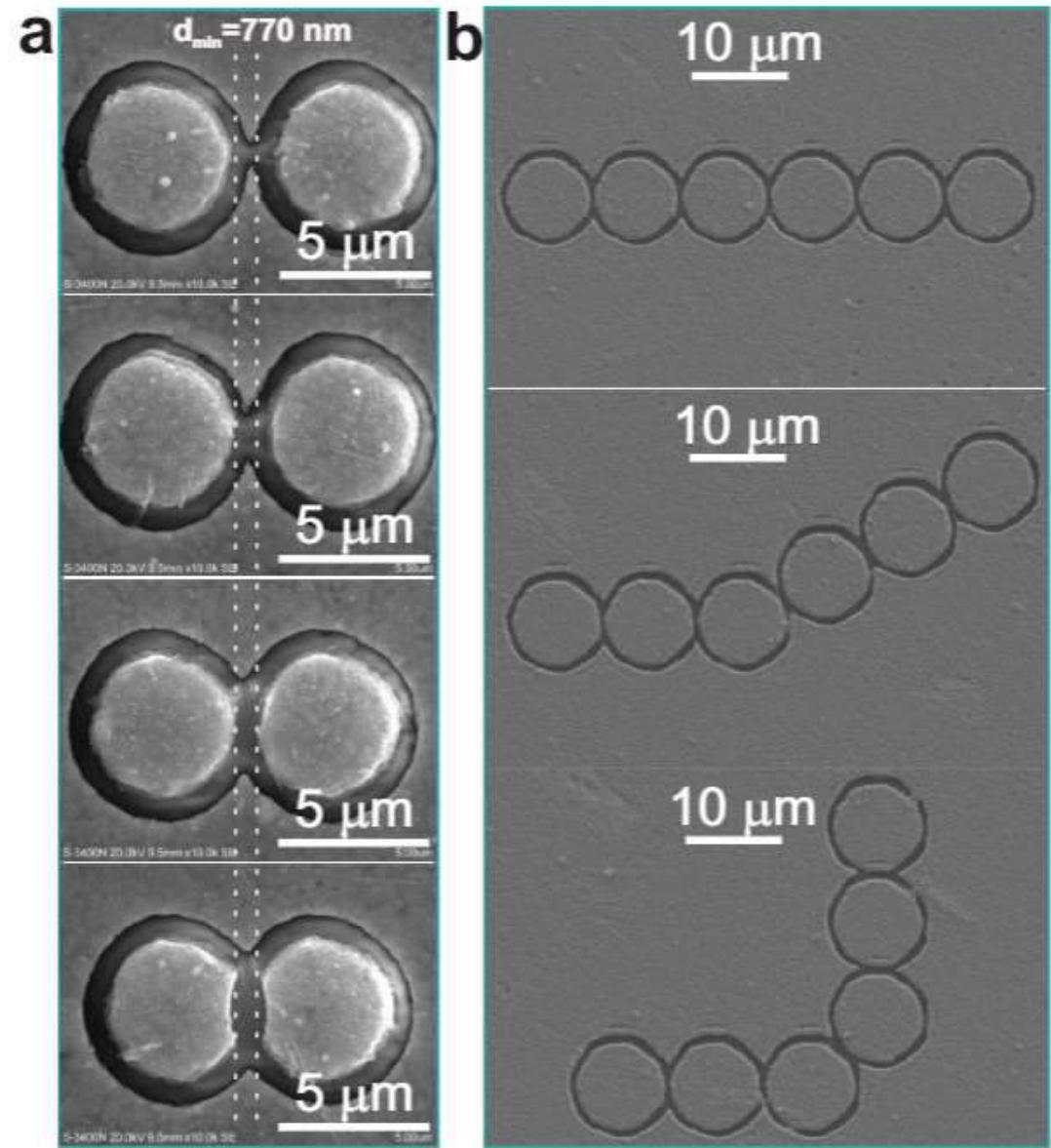
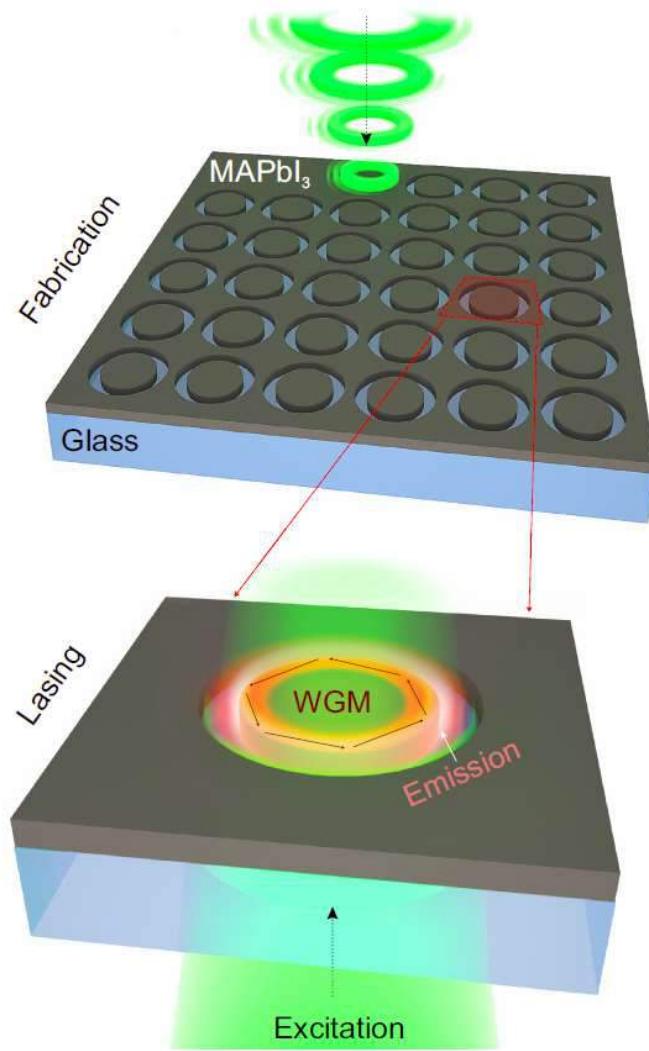
CsPbBr₃

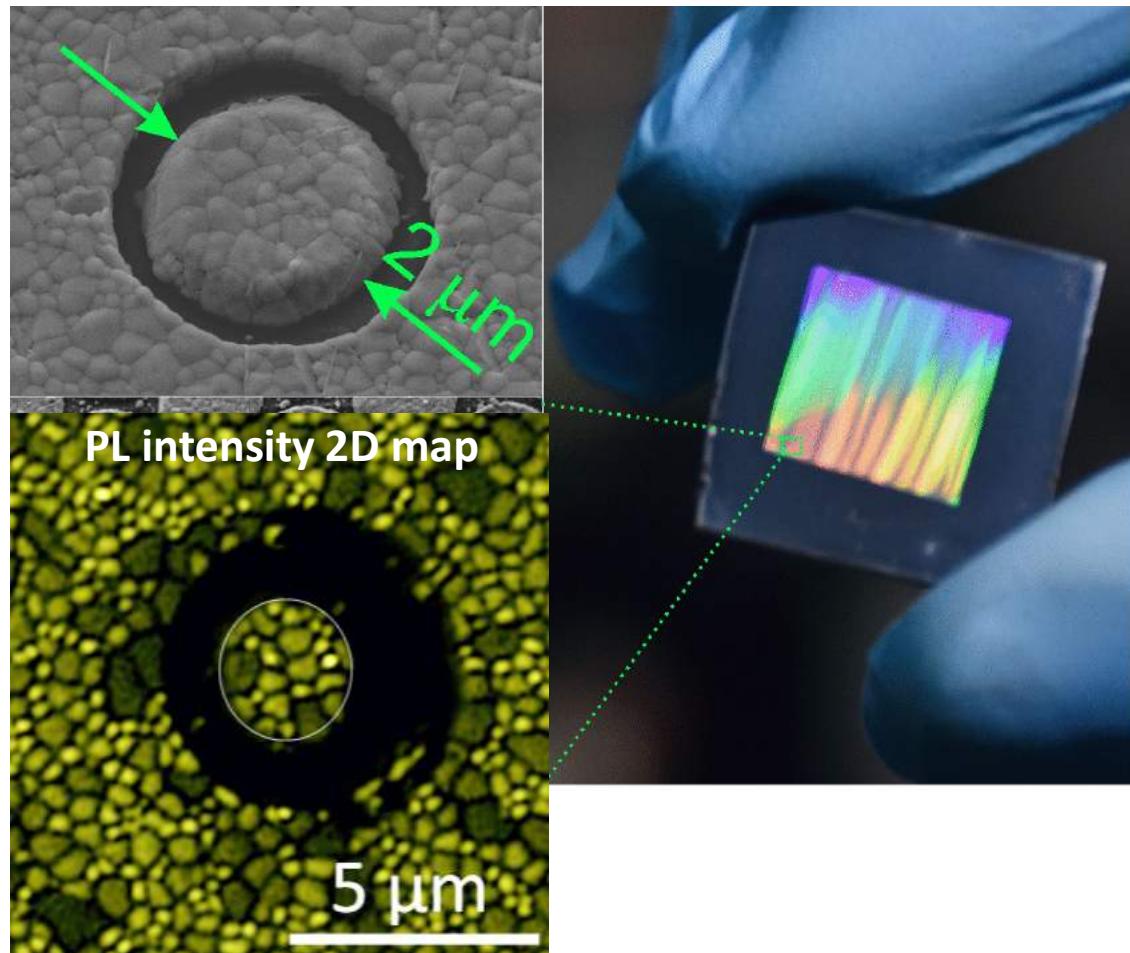


Problem: difficult to control the position!

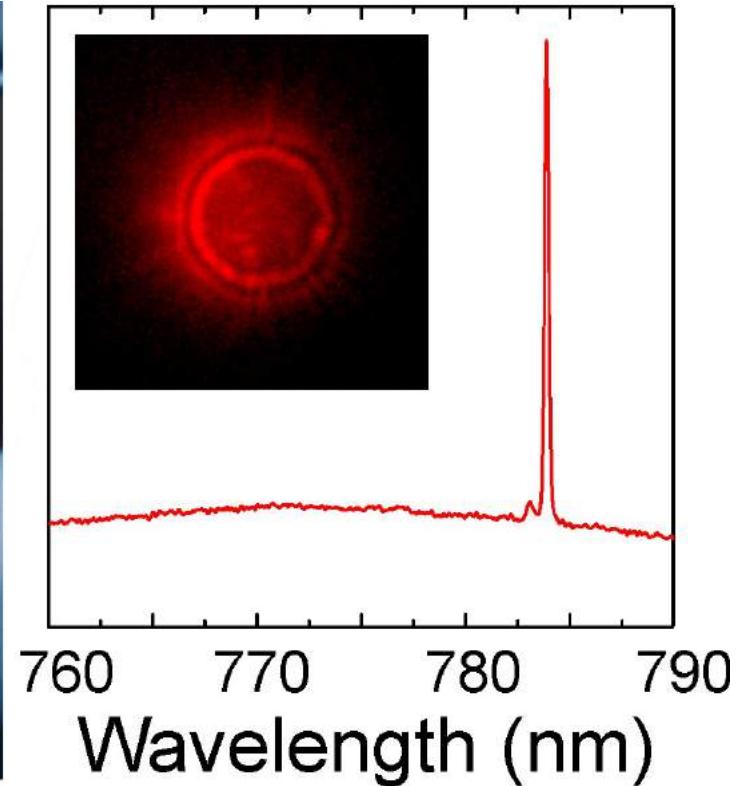


Laser printing of perovskite lasers

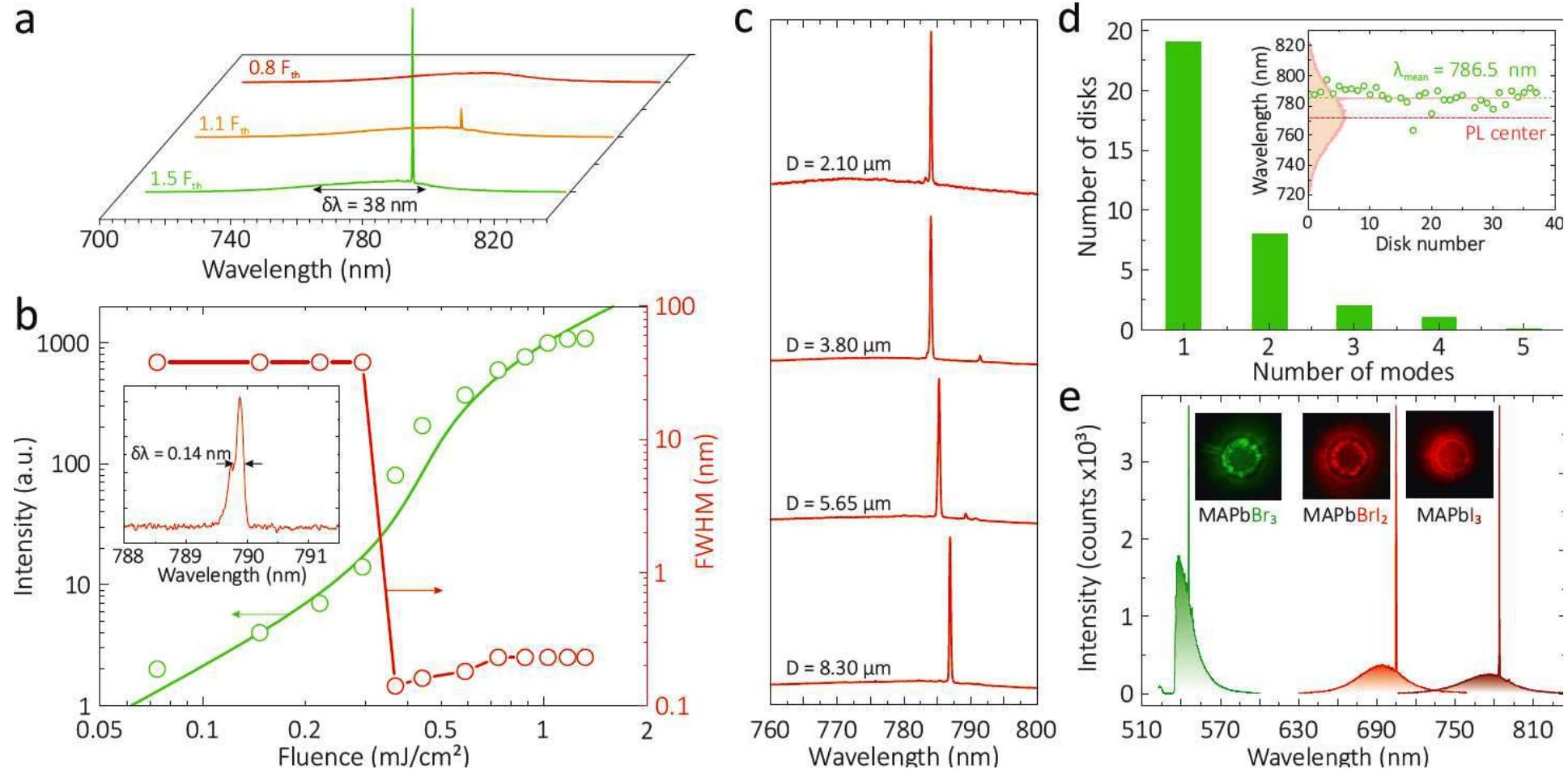




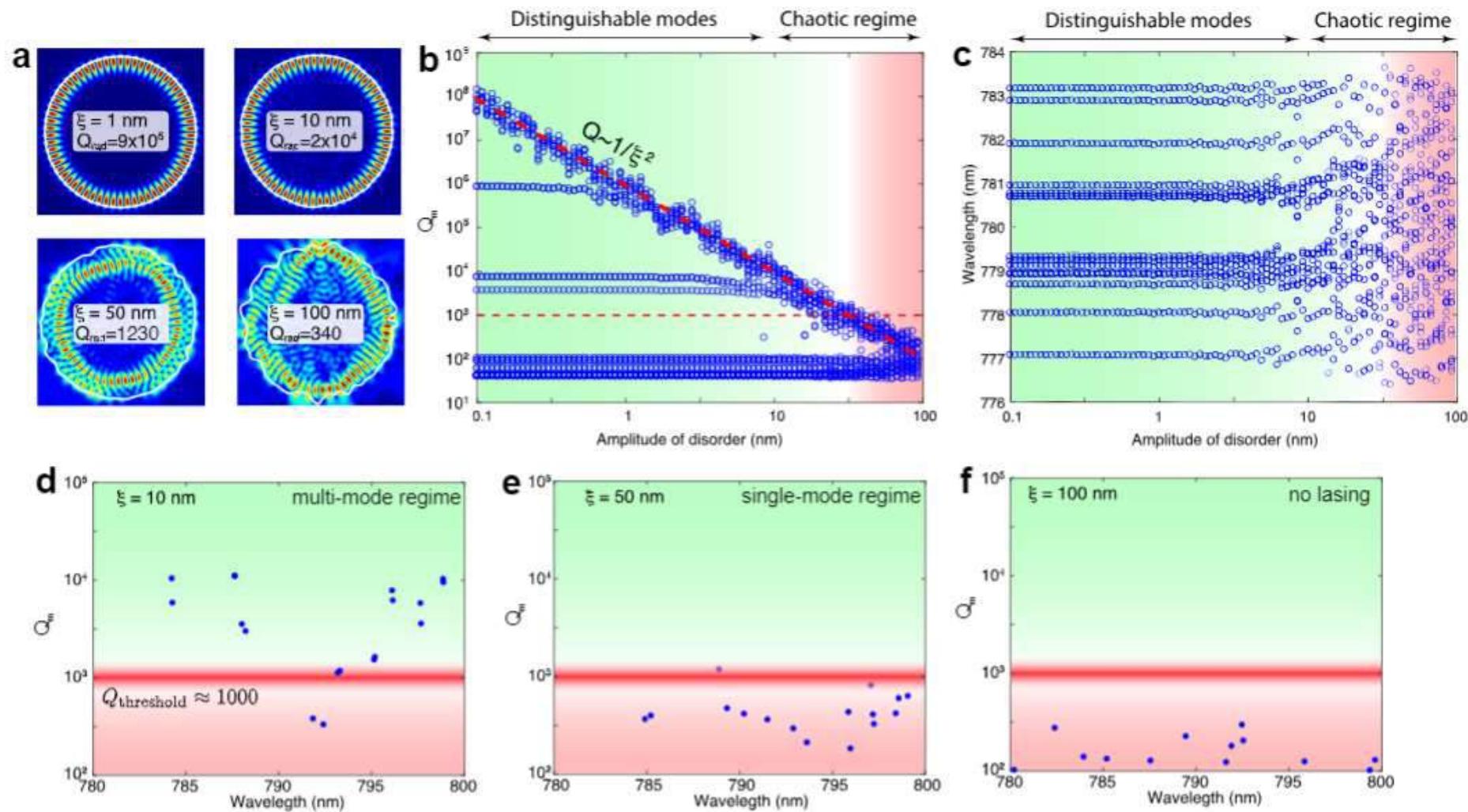
MAPbI₃



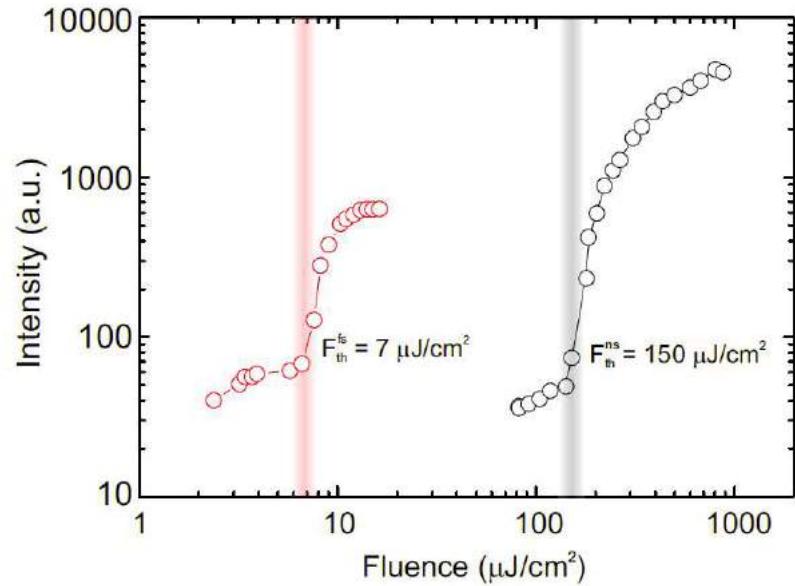
Perovskite is a defect-tolerant material!



ns-threshold: $\sim 200 \mu\text{J}/\text{cm}^2$
fs-threshold: $< 10 \mu\text{J}/\text{cm}^2$

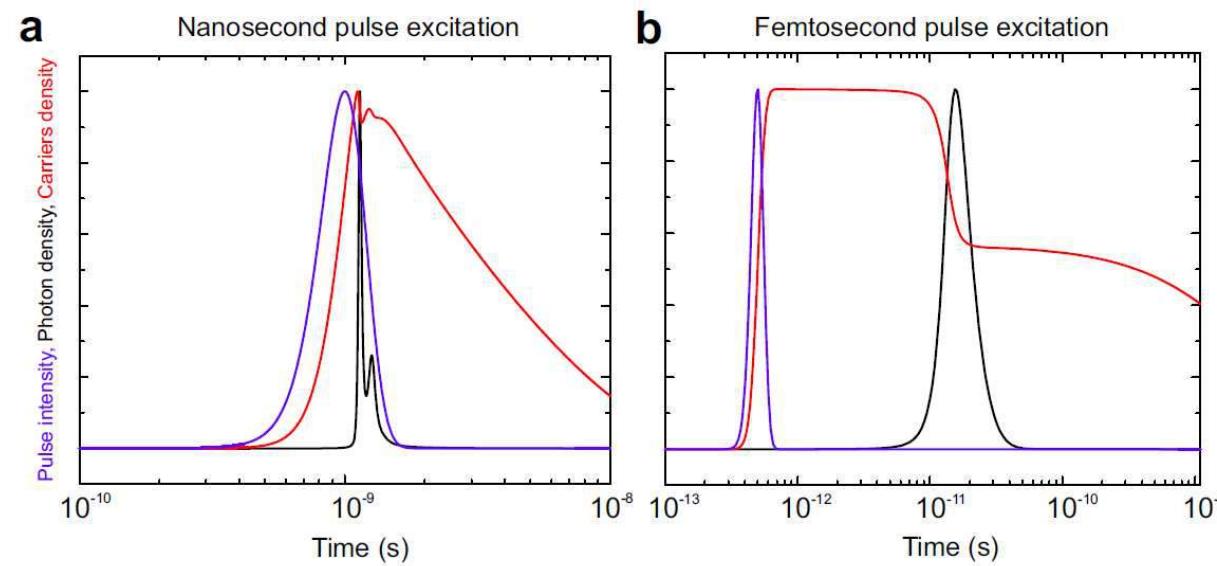


Roughness selects the WGM modes



$$\frac{dn}{dt} = \eta_p \frac{P}{\hbar\omega_p V_a} - R_{nr}(n) - R_{sp}(n) - R_{st}(n)s$$

$$\frac{ds}{dt} = -\frac{s}{\tau_p} + \Gamma\beta_{sp}R_{sp}(n) + \Gamma R_{st}(n)s,$$





- ✓ Reversibly tunable perovskite nanoantennas
Tiguntseva et al. *Nano Lett.* 18 (2), 1185-1190 (2018)
Tiguntseva et al. *Nano Lett.* 18 (9), 5522-5529 (2018)
- ✓ Extremely fast method of nanowire lasers synthesis
Pushkarev et al. *ACS Appl. Mater. Interfaces*, 11 (1), 1040–1048 (2019)
- ✓ Large-scale laser printing of perovskite microlasers
Zhizhchenko et al. *ACS Nano* doi:10.1021/acsnano.8b08948 (2019)
- ✓ All-dielectric nanolasers...
Tiguntseva et al. (in progress)

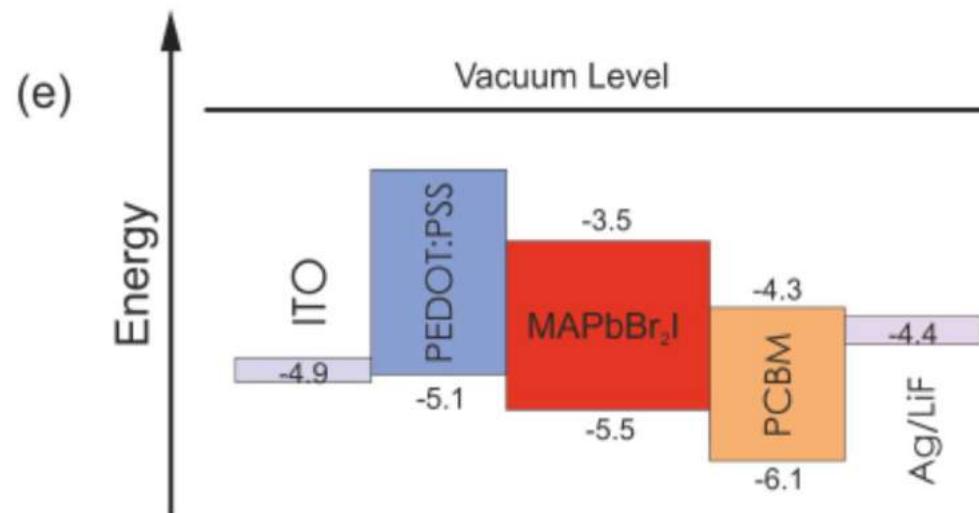
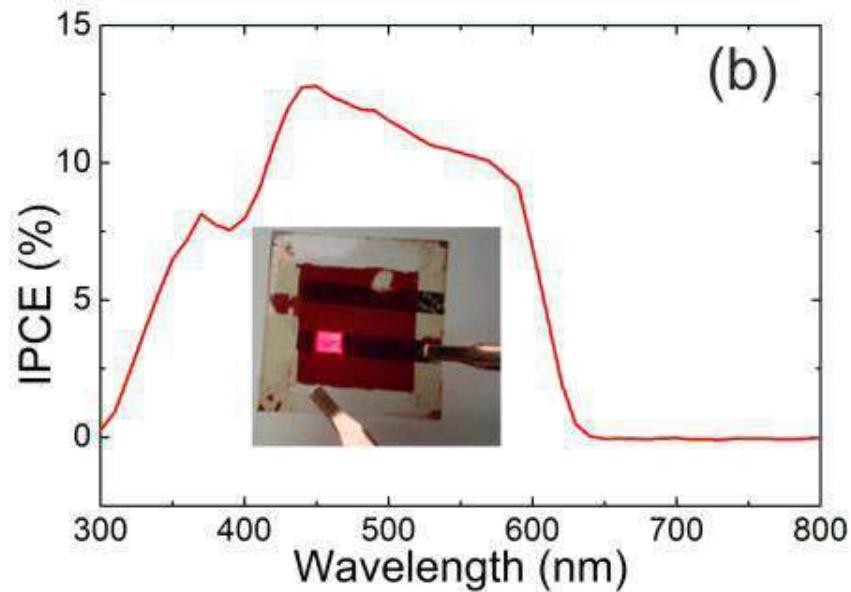
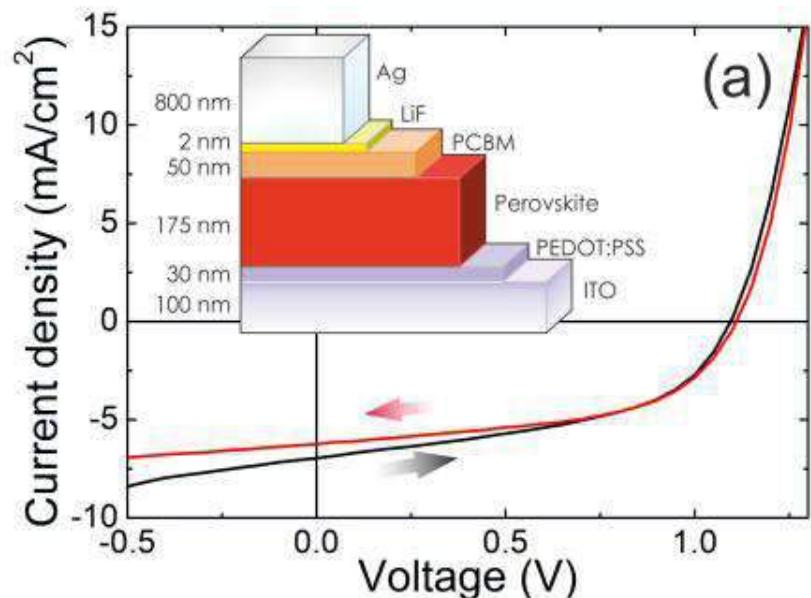
Review: Makarov et al, “Halide-Perovskite Resonant Nanophotonics”
Advanced Optical Materials, 7 (1), 1800784 (2019)



ITMO UNIVERSITY

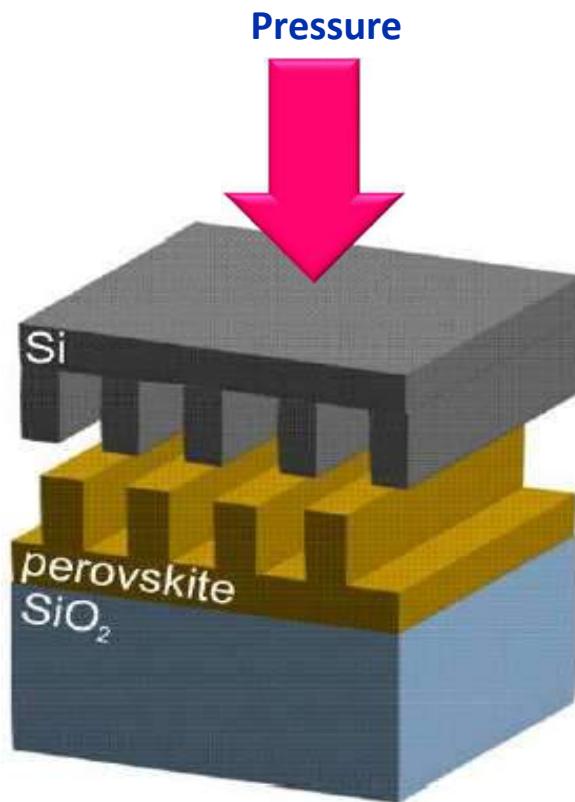


Thank you for your attention!

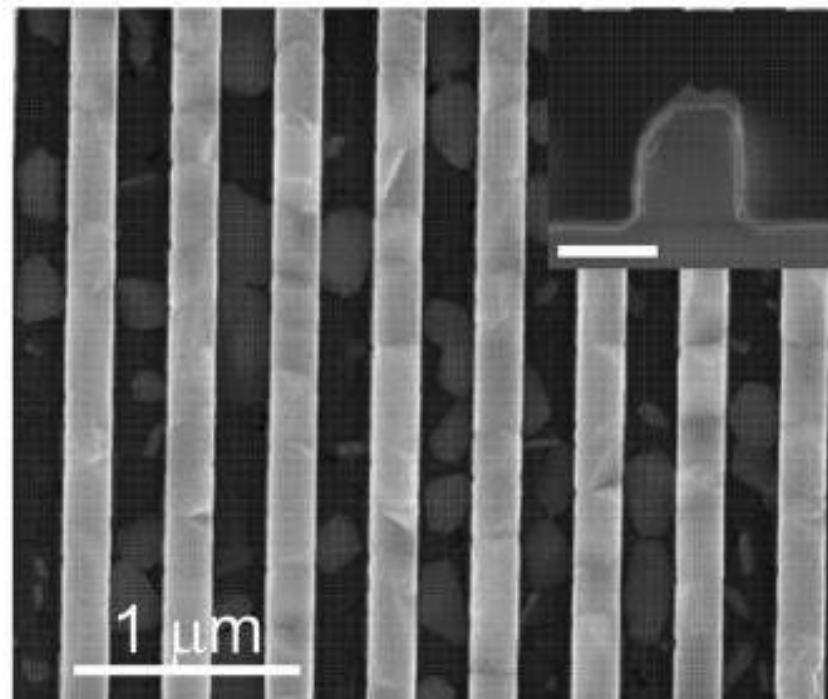




Nanoimprint lithography



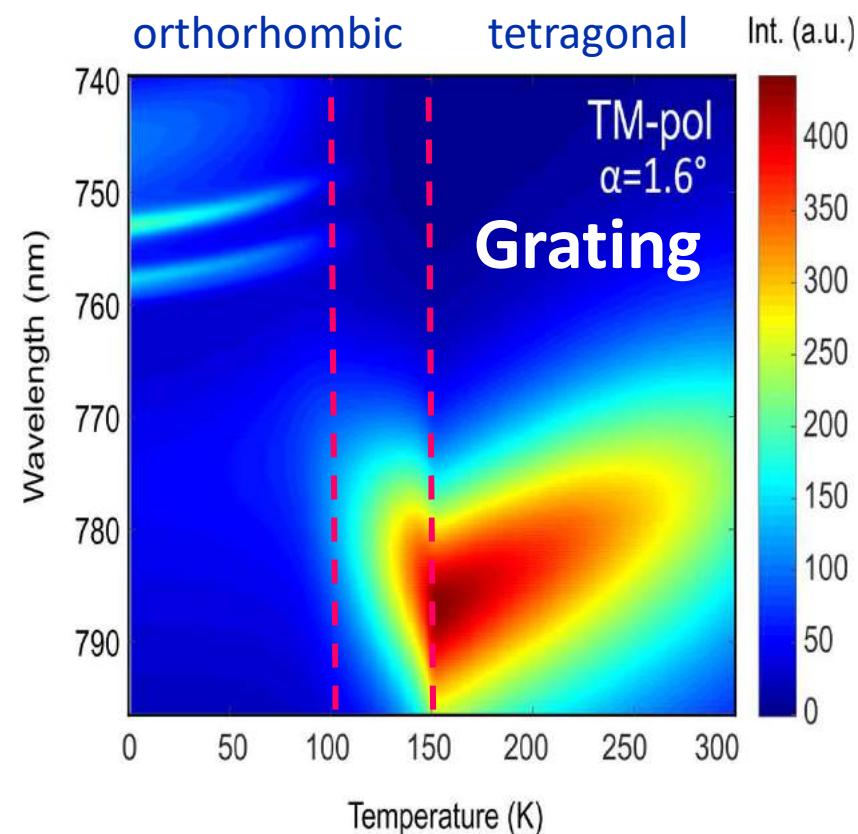
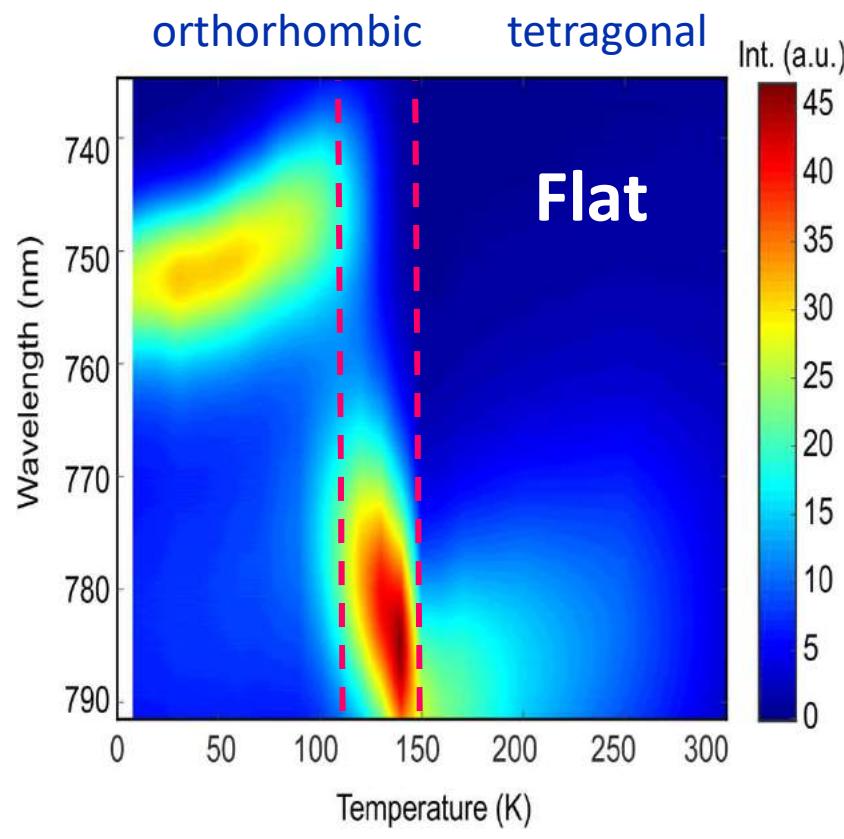
Scheme of
nanoimprint
lithography process

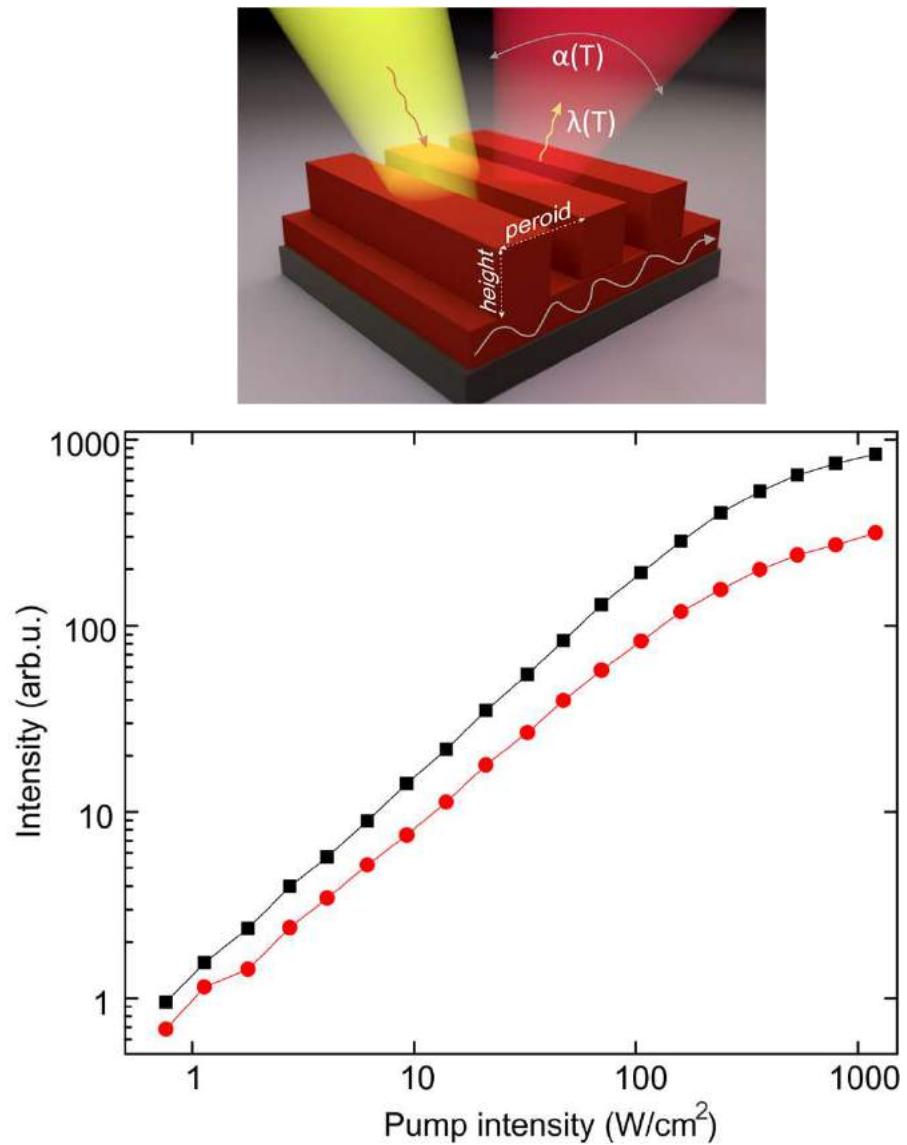
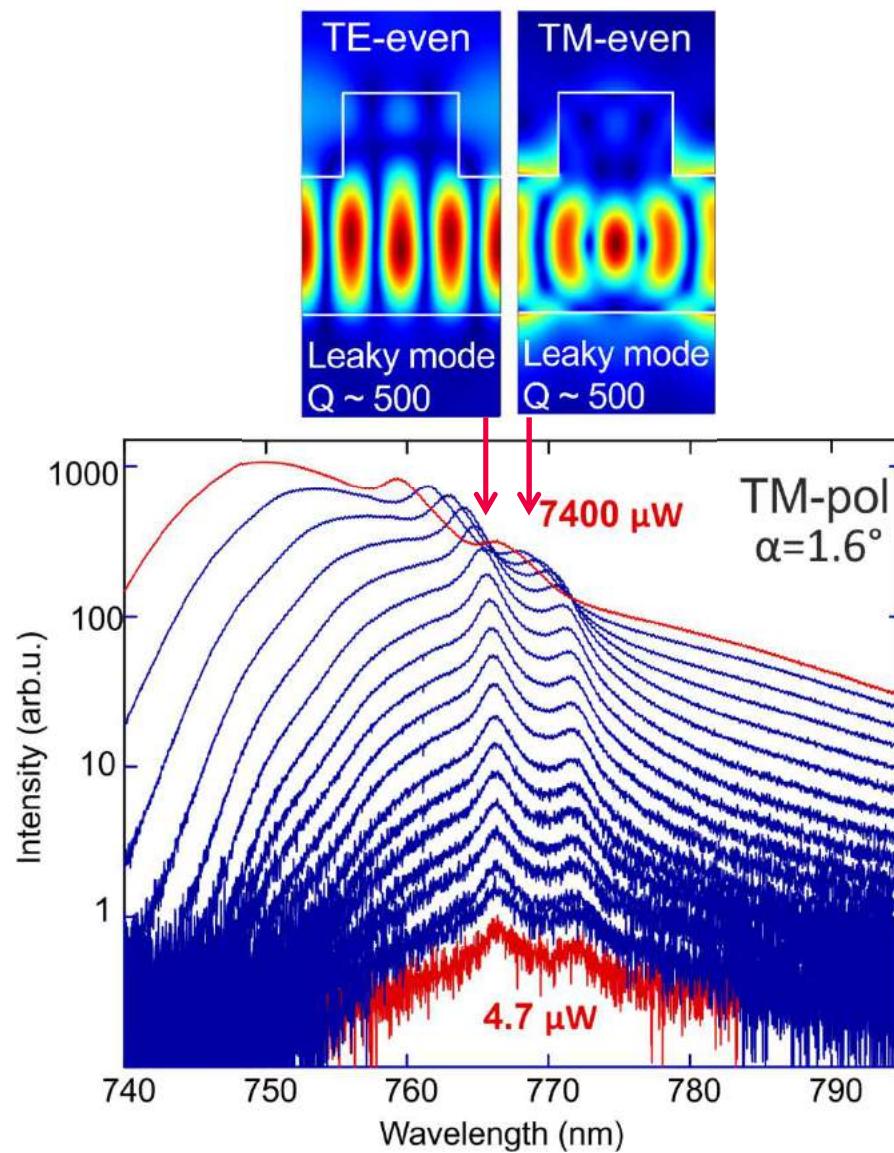


SEM image of film structure



MAPbI₃







ITMO UNIVERSITY

metalab.ifmo.ru

nature
photonics

LETTERS

<https://doi.org/10.1038/s41566-017-0047-6>

Continuous-wave lasing in an organic-inorganic lead halide perovskite semiconductor

Yufei Jia¹, Ross A. Kerner², Alex J. Grede¹, Barry P. Rand² and Noel C. Giebink^{1*}

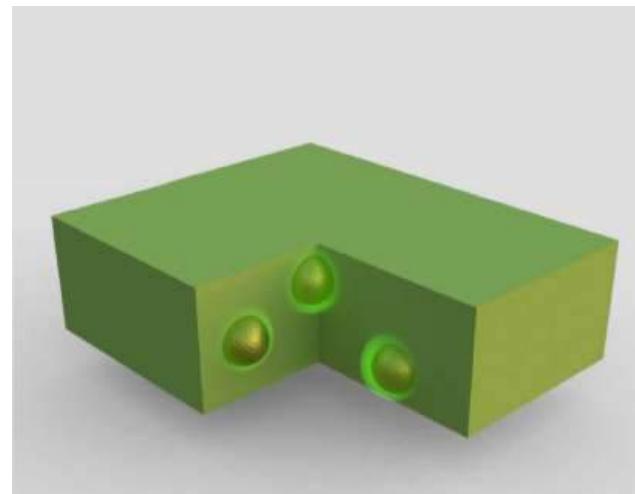
Hybrid organic-inorganic perovskites have emerged as promising gain media for tunable, solution-processed semiconductor lasers. However, continuous-wave operation has not been achieved so far¹⁻³. Here, we demonstrate that optically pumped continuous-wave lasing can be sustained above threshold excitation intensities of $\sim 17 \text{ kW cm}^{-2}$ for over an hour in methylammonium lead iodide (MAPbI_3) distributed feedback lasers that are maintained below the MAPbI_3 tetragonal-to-orthorhombic phase transition temperature of $T \approx 160 \text{ K}$. In contrast with the lasing death phenomenon that occurs for pure tetragonal-phase MAPbI_3 at $T > 160 \text{ K}$ (ref. ⁴), we find that continuous-wave gain becomes possible at $T \approx 100 \text{ K}$ from tetragonal-phase inclusions that are photogenerated by the pump within the normally existing hexagonal

tetragonal phase inclusions may act as charge carrier sinks within the larger-bandgap orthorhombic phase host matrix, enhancing population inversion in a fashion analogous to host-guest organic-semiconductor gain media and inorganic quantum wells^{13,14}. These results suggest a general strategy to design perovskite gain media for c.w. lasing and represent a key step towards the ultimate goal of a perovskite laser diode.

Figure 1 explores the amplified spontaneous emission (ASE) gain dynamics of a 120-nm-thick MAPbI_3 film deposited on a sapphire substrate using an InGaN pump diode ($\lambda_p = 445 \text{ nm}$, intensity $I_p = 37.5 \text{ kW cm}^{-2}$, 920-ns-long pulses at 100 Hz repetition rate) and a streak camera. In Fig. 1a, at a substrate temperature of $T = 169 \text{ K}$, tetragonal-phase ASE is observed immediately following pump turn on but ceases within $\sim 100 \text{ ns}$, giving way to incoher-

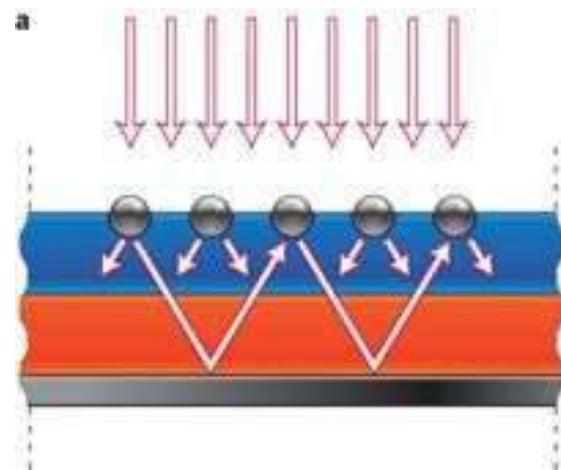


Perovskite solar cells with Si nanoparticles

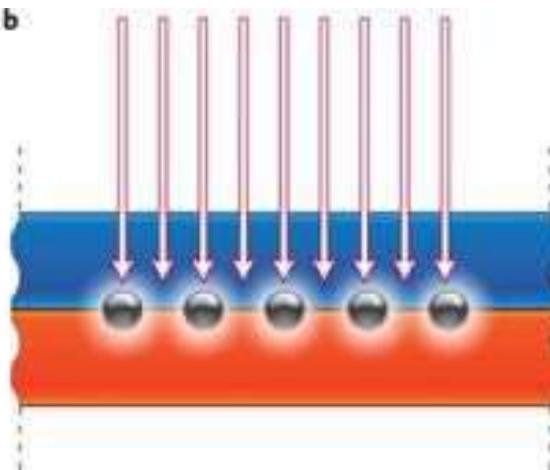




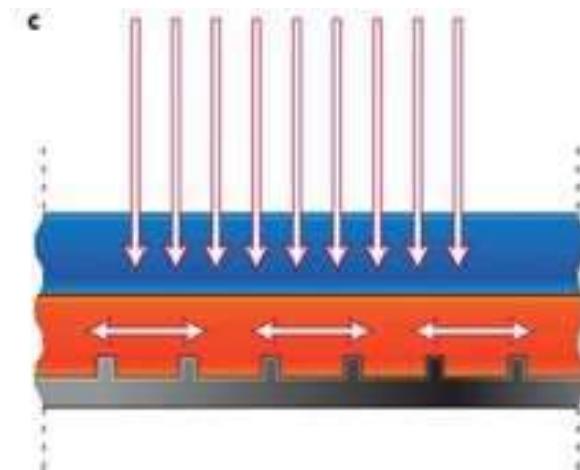
Plasmonics for improved photovoltaic devices



scattering



near-field
enhancement



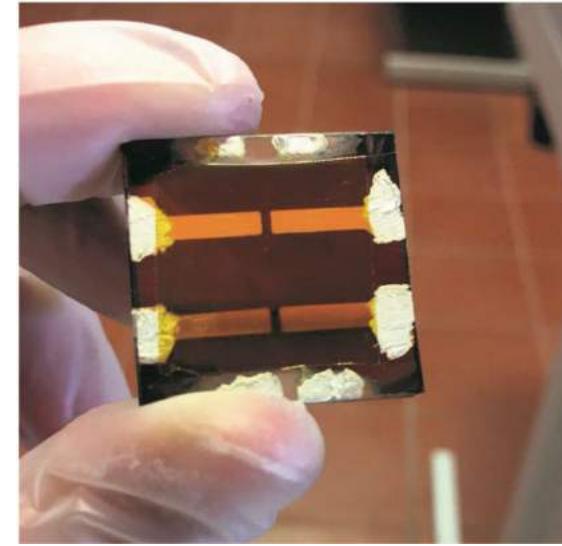
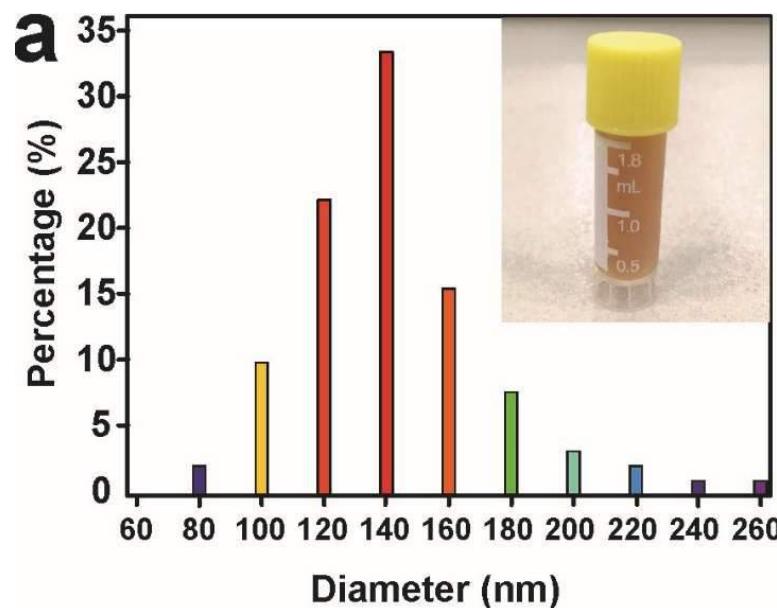
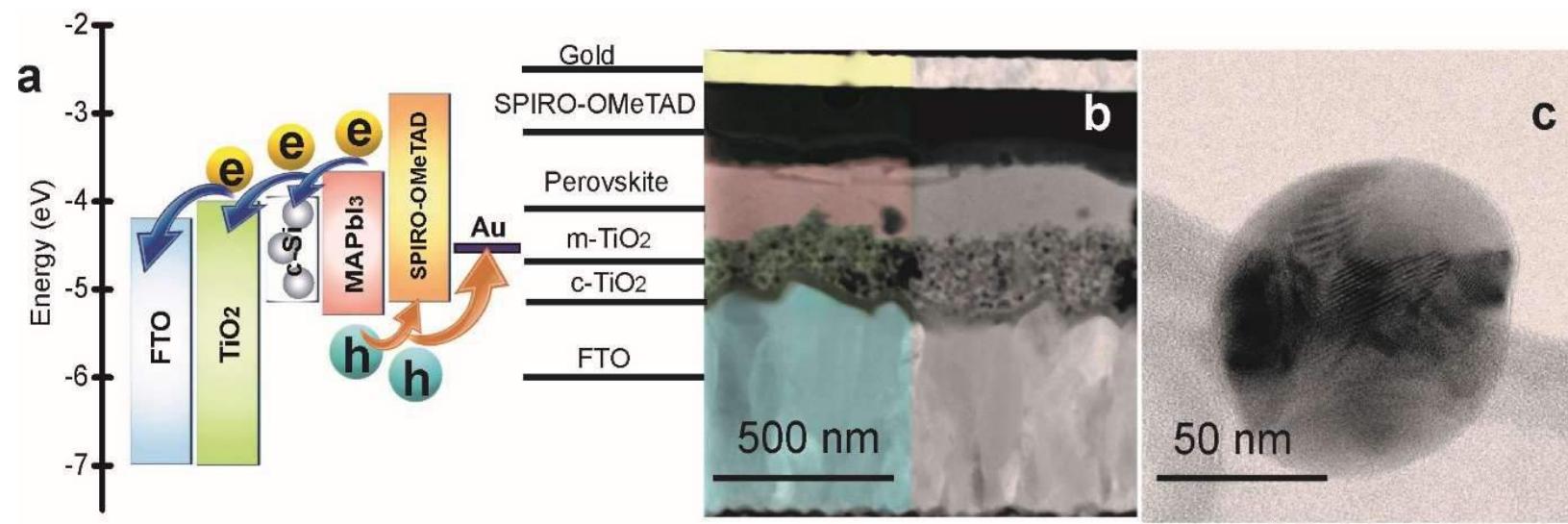
waveguiding



Resonant nanoparticles, shape (diameter)	Efficiency (%) / Fill factor (%)
Si, nanospheres, (100-200 nm)	18.8/79
Au@TiO ₂ , nanospheres (80nm)	18.2/75.5
Au@SiO ₂ , nanospheres (14 nm)	17.6/78.2
Au@SiO ₂ , nanorods (15×37 nm)	17.6/77.3
Au@TiO ₂ , nanorods (5×40) nm	16.8/74.7
Au, nanospheres (40 nm)	16.2/76
Au, nanospheres (40 nm)	16.1/68
Au@TiO ₂ , nanospheres (60 nm)	14.9/70
Au@SiO ₂ , nanospheres (45 nm) / nanorods (8×55 nm)	13.7/68
Ag@TiO ₂ , nanospheres (40 nm)	13.7/67
Au, nanostars (30 nm)	13.7/72.1 (regular) 8.7/71.2 (invert)
Au@SiO ₂ , nanospheres (100 nm)	11.4/64

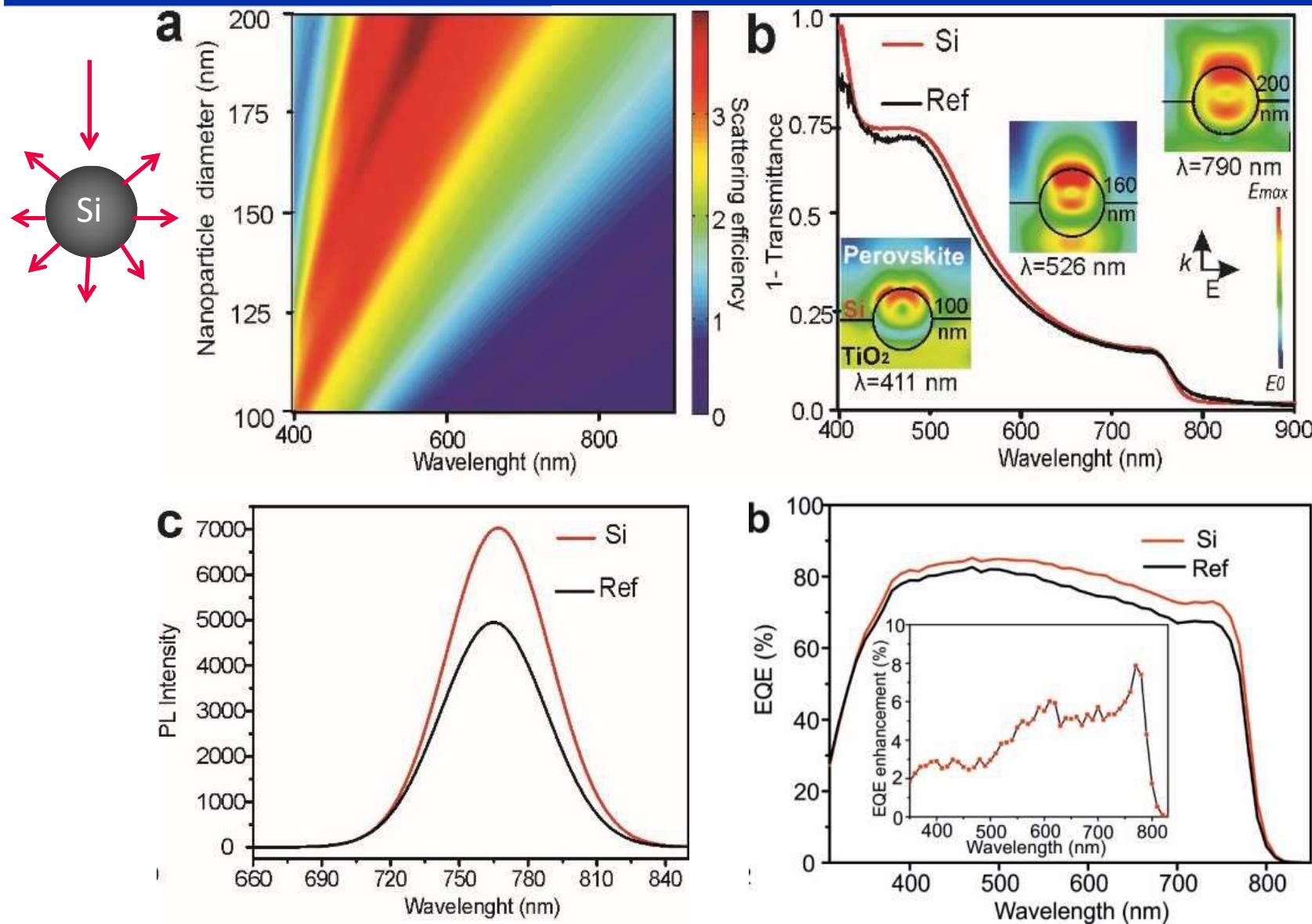


Silicon NPs for pero-PV





Silicon NPs for pero-PV





Silicon NPs for pero-PV

