# Light Engineering in New Materials

How material science can help in realizing new efficient incoherent and coherent light sources

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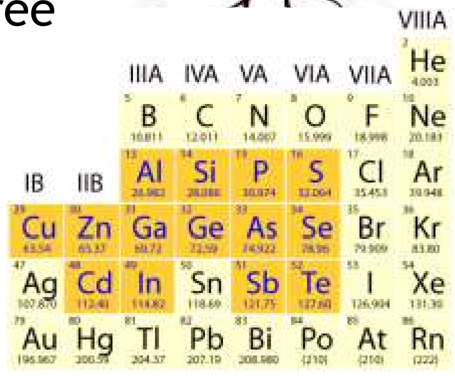
# Outline

- A little bit of history
- Band-gap engineering
- Epitaxial growth
- Chemical synthesis
- Perovskites
- A look to the future

# A little bit of history: 150 years from the Mendeleev Table

The semiconductor tree

The Mendeleev table is the tree principal root



# The recognition of material science relevance

The nanostructures and the superconductors

## The Nobel Prize in Physics 1973

Photo from the Nobel Foundation archive.
Leo Esaki
Prize share: 1/4

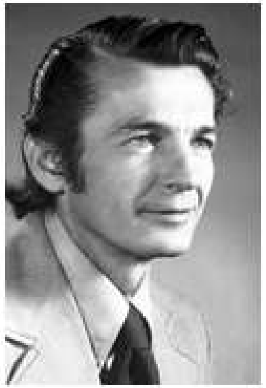


Photo from the Nobel Foundation archive.
Ivar Giaever
Prize share: 1/4

Photo from the Nobel Foundation archive.
Brian David Josephson
Prize share: 1/2

The Nobel Prize in Physics 1973 was divided, one half jointly to Leo Esaki and Ivar Giaever "for their experimental discoveries regarding tunneling phenomena in semiconductors and superconductors, respectively" and the other half to Brian David Josephson "for his theoretical predictions of the properties of a supercurrent through a tunnel barrier, in particular those phenomena which are generally known as the Josephson effects."

## Heterostructures and integrated circuit

### The Nobel Prize in Physics 2000

"for basic work on information and communication technology"

"for developing semiconductor heterostructures used in high-speed- and opto-electronics"

"for his part in the invention of the integrated circuit"

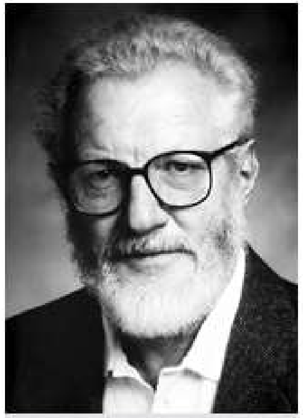
**Zhores I. Alferov**

1/4 of the prize

Russia

A.F. Ioffe Physico-Technical Institute
St. Petersburg, Russia

b. 1930



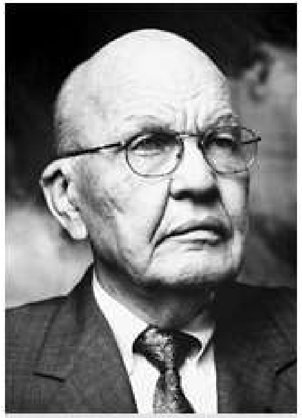
**Herbert Kroemer**

1/4 of the prize

Federal Republic of Germany

University of California
Santa Barbara, CA, USA

b. 1928



**Jack S. Kilby**

1/2 of the prize

USA

Texas Instruments
Dallas, TX, USA

b. 1923
d. 2005

# The CCD

Physics

## The Nobel Prize in Physics 2009

"for groundbreaking achievements concerning the transmission of light in fibers for optical communication"

"for the invention of an imaging semiconductor circuit – the CCD sensor"

Photo: U. Montan

**Charles K. Kao**

1/2 of the prize

Standard Telecommunication Laboratories
Harlow, United Kingdom;
Chinese University of Hong Kong
Hong Kong, China

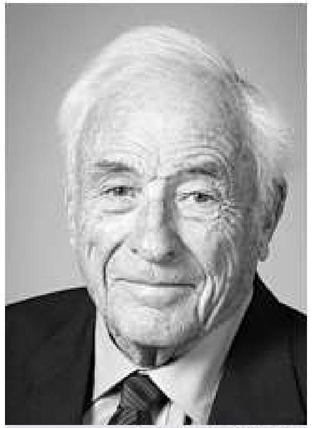


Photo: U. Montan

**Willard S. Boyle**

1/4 of the prize

Bell Laboratories
Murray Hill, NJ, USA

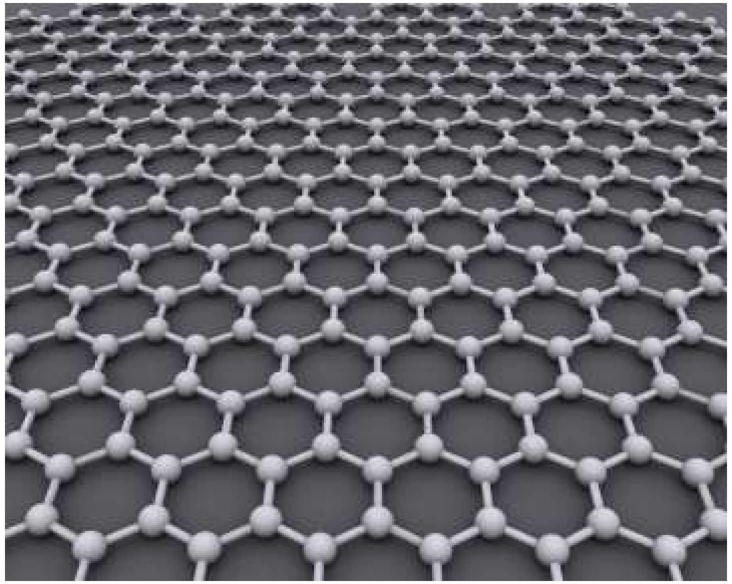
Photo: U. Montan

**George E. Smith**

1/4 of the prize

Bell Laboratories
Murray Hill, NJ, USA

# The Graphene: the perfect lattice

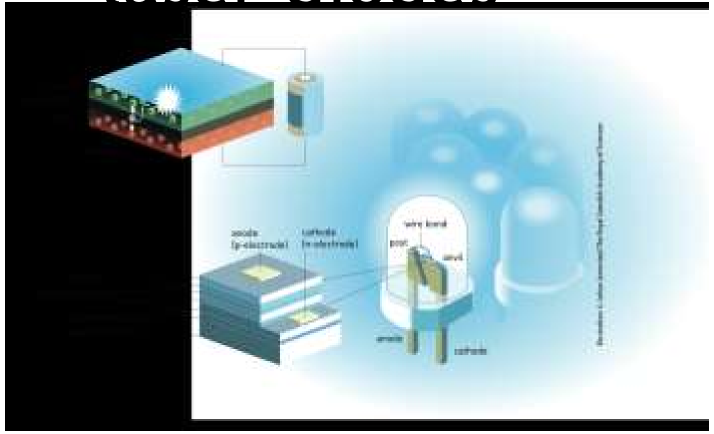


## The Nobel Prize in Physics 2010

Andre Geim and Konstantin Novoselov

"for groundbreaking experiments regarding the two-dimensional material graphene"

# The blue/white laser diodes



# The Nobel Prize in Physics 2014

Photo: A. Mahmoud

**Isamu Akasaki**

**Prize share: 1/3**

Photo: A. Mahmoud

**Hiroshi Amano**

**Prize share: 1/3**

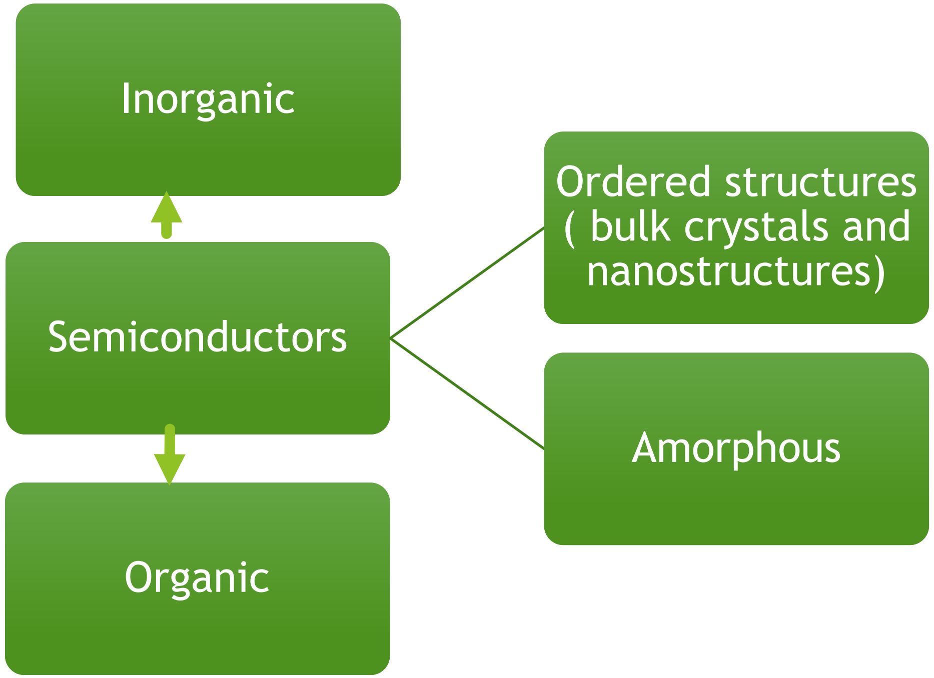
Photo: A. Mahmoud

**Shuji Nakamura**

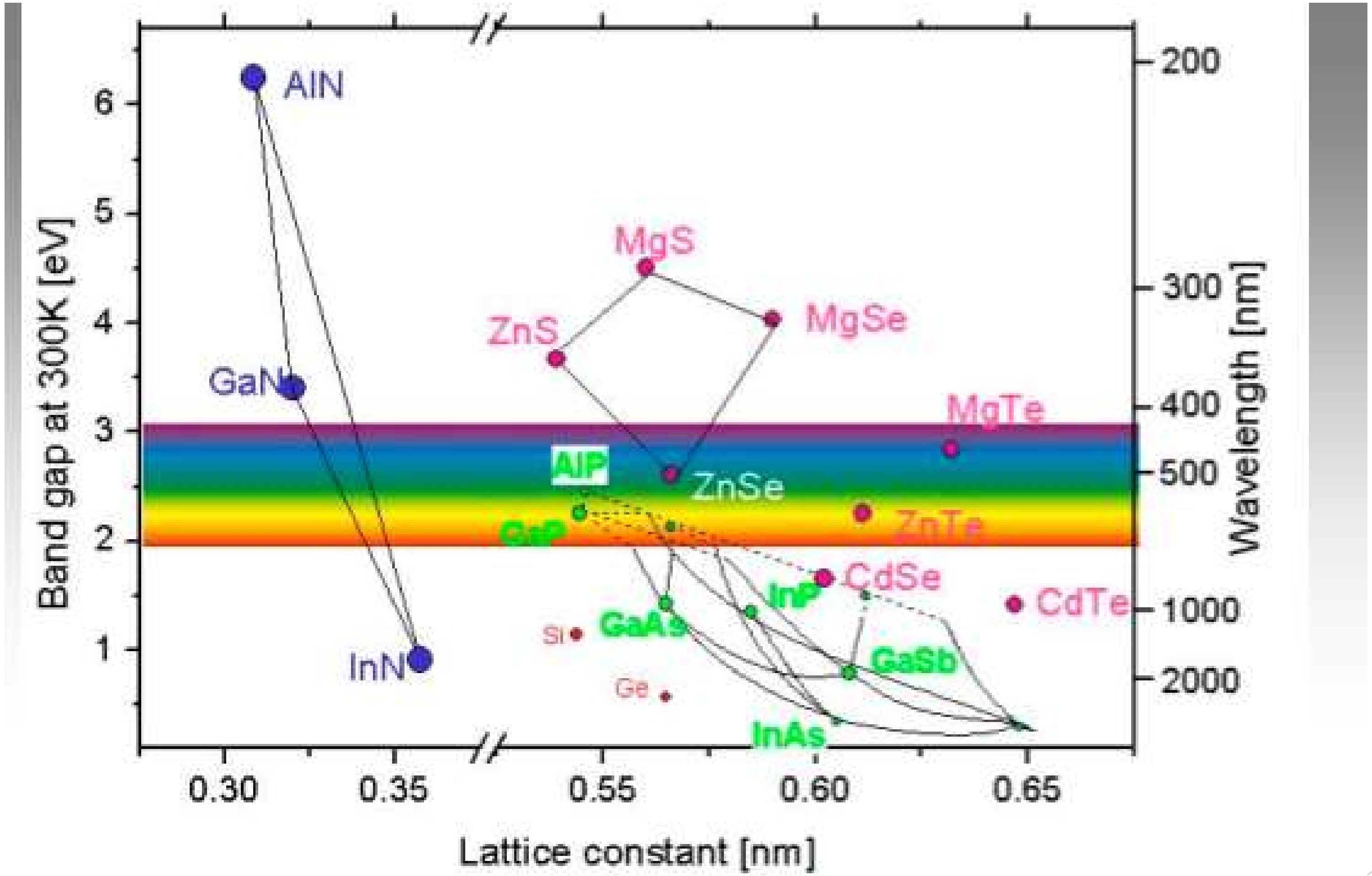
**Prize share: 1/3**

The Nobel Prize in Physics 2014 was awarded jointly to Isamu Akasaki, Hiroshi Amano and Shuji Nakamura *"for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources".*

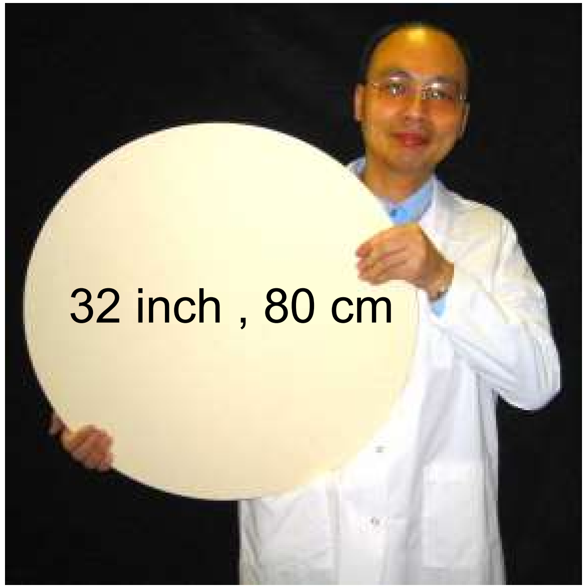
# The materials for opto-devices



# The Rosetta Stone of Semiconductors



# The King of Semiconductors for electronics: Silicon

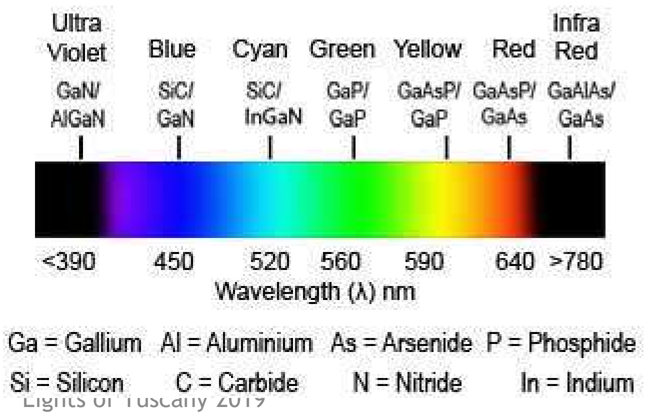



Unfortunately Si is very bad for light emitters being an indirect band-gap semiconductor, so it is hard to have electrons and holes recombining in a radiative way !

# The Kings of Semiconductors for light emitters : III-V and III-Nitrides

In,Ga,Al Arsenide and Nitride Alloys  with a band gap value ranging from 0.8 to 4 eV

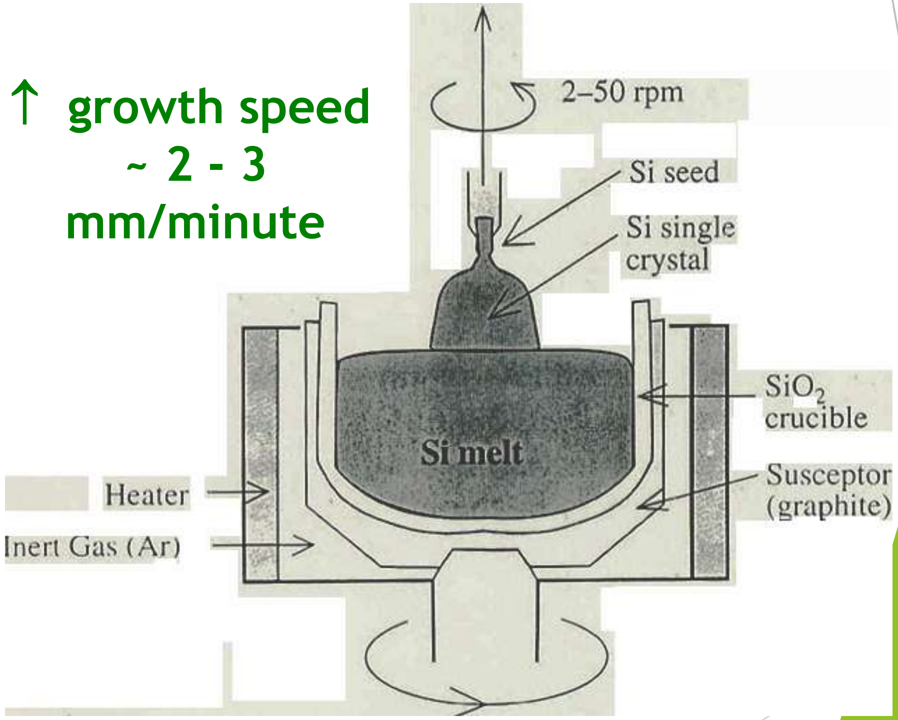
We can realize a device emitting light from 1.55 μm (  perfect for telecomm) and 300 nm ( perfect for UV- lithography and blue-rays, UV curing, etc.). White LEDs are realized using nitride alloys.



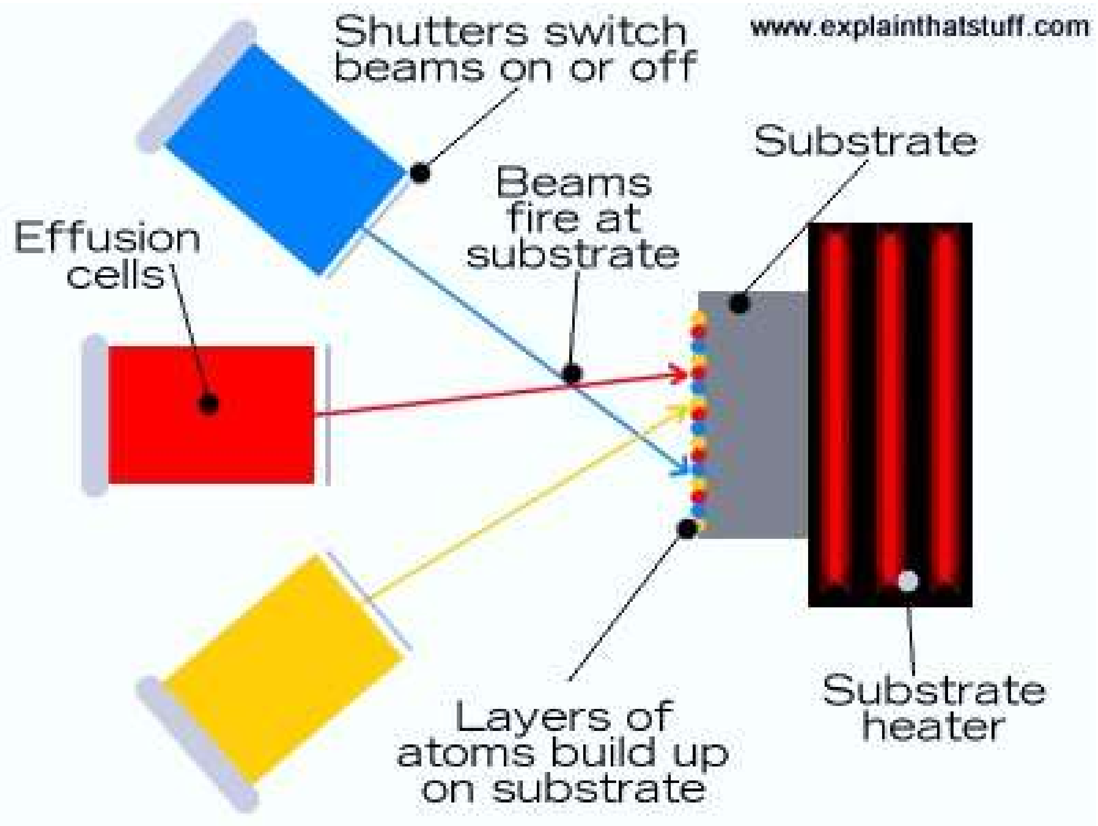

# How materials are realized?

- Czochralski growth (1916): very fast for big crystals : O and C common contaminants
- Epitaxial growth developed in late 1960s in Bell Labs

↑ growth speed ~ 2 - 3 mm/minute

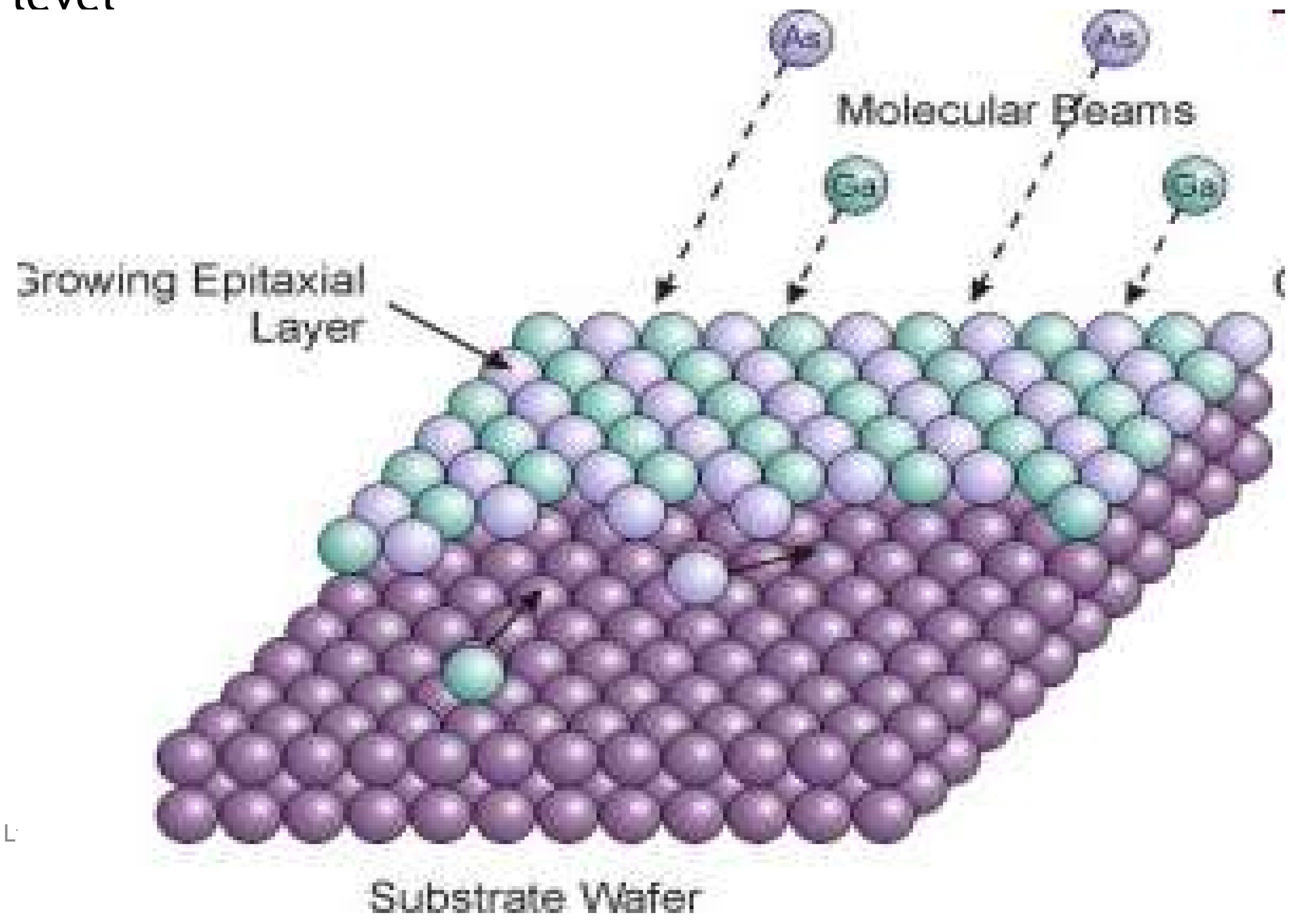


# Molecular Beam Epitaxy



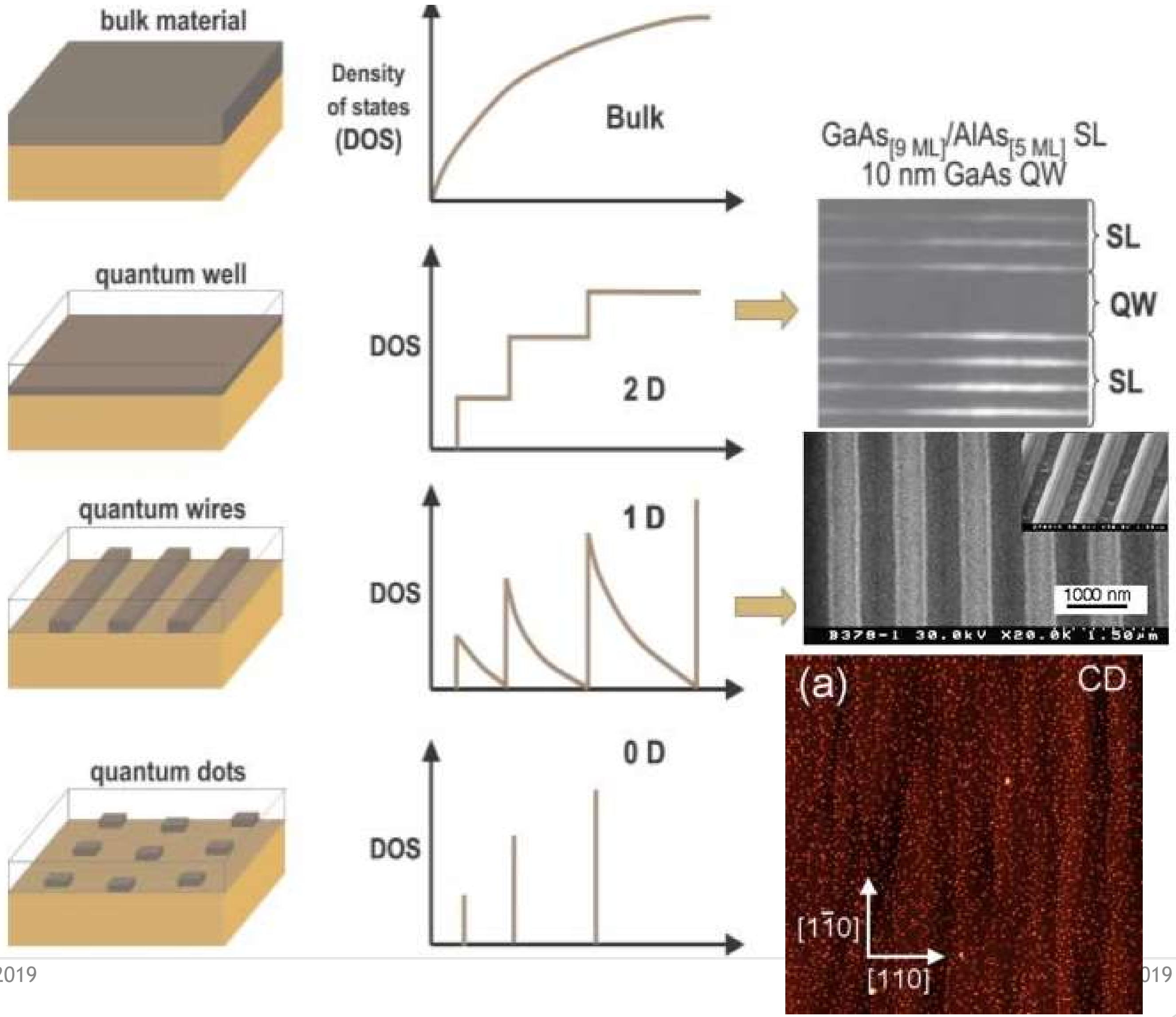
# Epitaxy can be by Molecular Beam, Chemical Vapour, Liquid Phase

Epitaxy means in “ growth in an ordered way”: epitaxial growth is therefore a growth with an high control of the deposition, at the atomic level



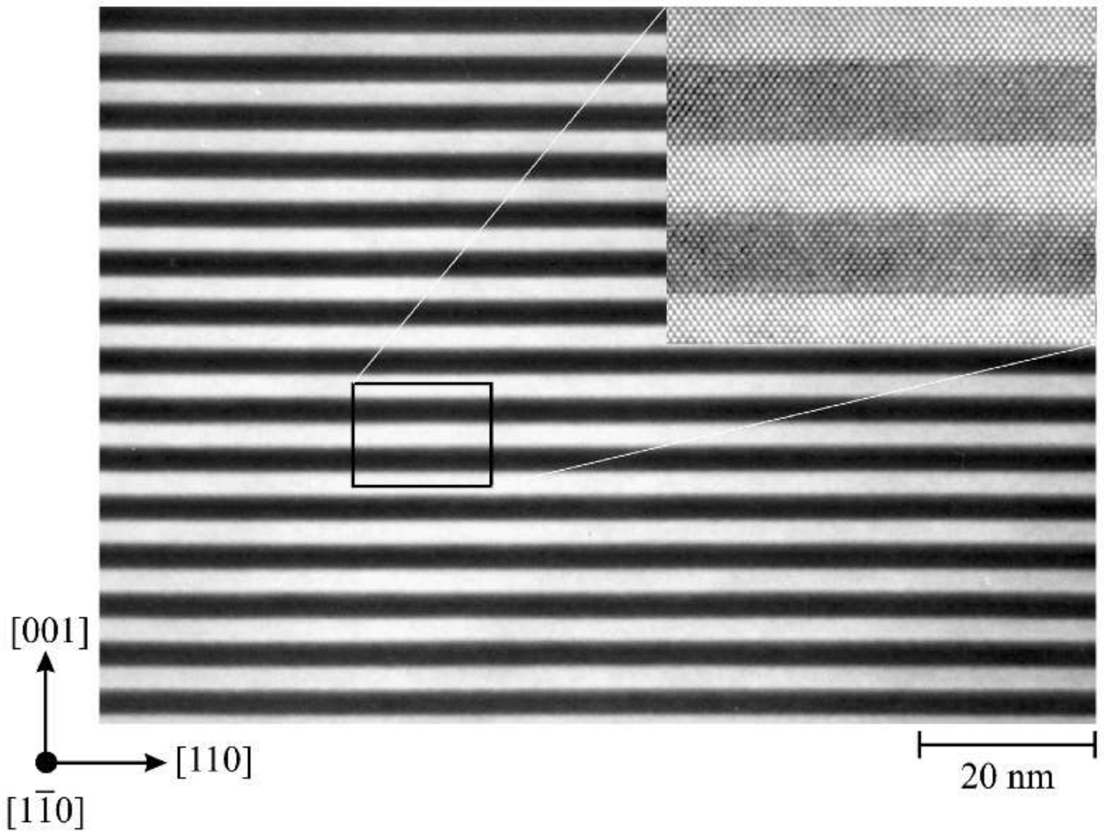

It requires same crystallographic lattice and “same” lattice constant  to avoid extended defects which are detrimental for the device operation

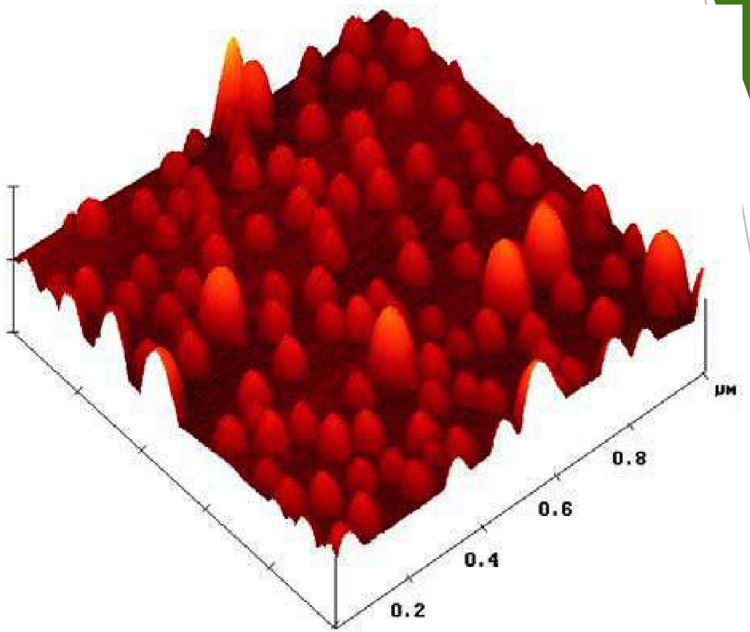
# But Nature can help: Self-assembled growth



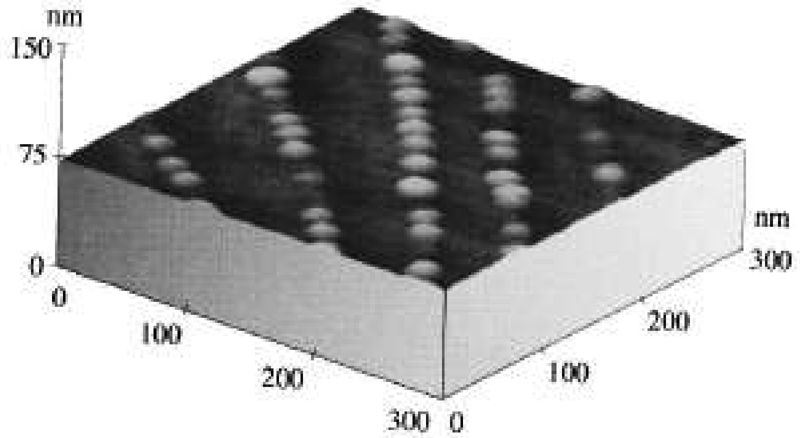
# Some results

A superlattice




Quantum dots



# What’s the meaning?

We can modify the electronic properties ( energy, band dispersion, band gap…) at the nanoscale ( few Angstrom up to tens of nm)

Quantum effects dominate and we can tailor the material properties the way we prefer

# So very nice results but…..
# Highly expensive techniques

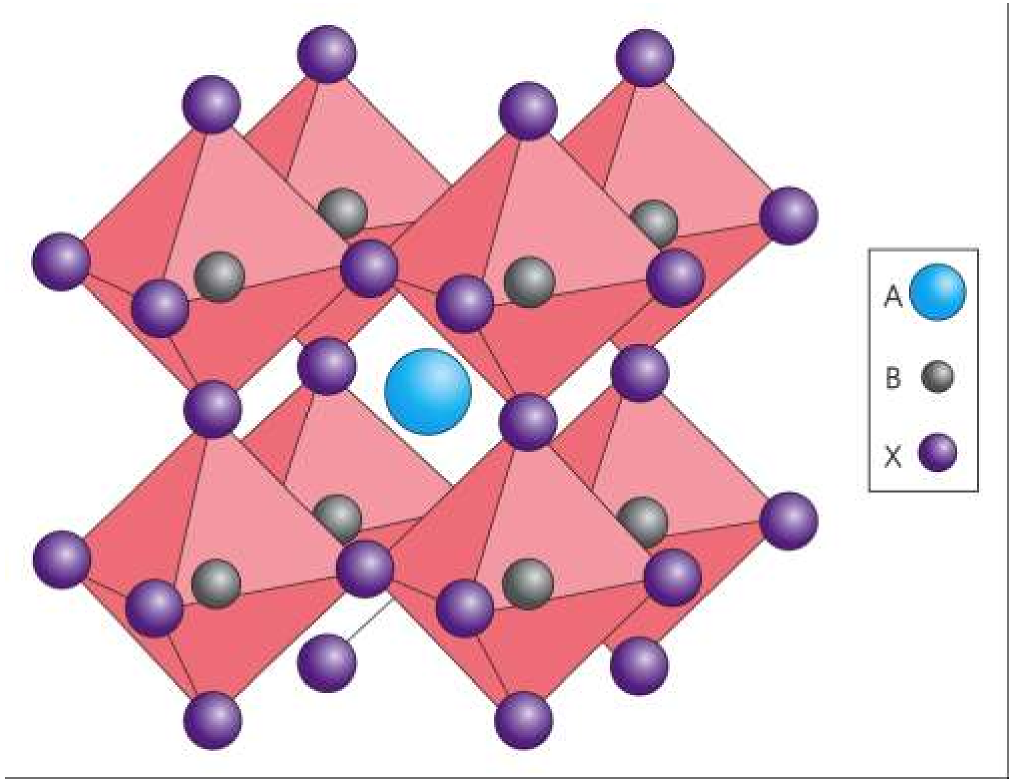
As alternative:

## Chemical synthesis

# Advantages of chemical synthesis

- Low cost synthesis and processing
- High tunability of band-gap
- Easier integration in photonic structures

# The promising class of materials: Perovskites




Same class of material as $CaTiO_3$

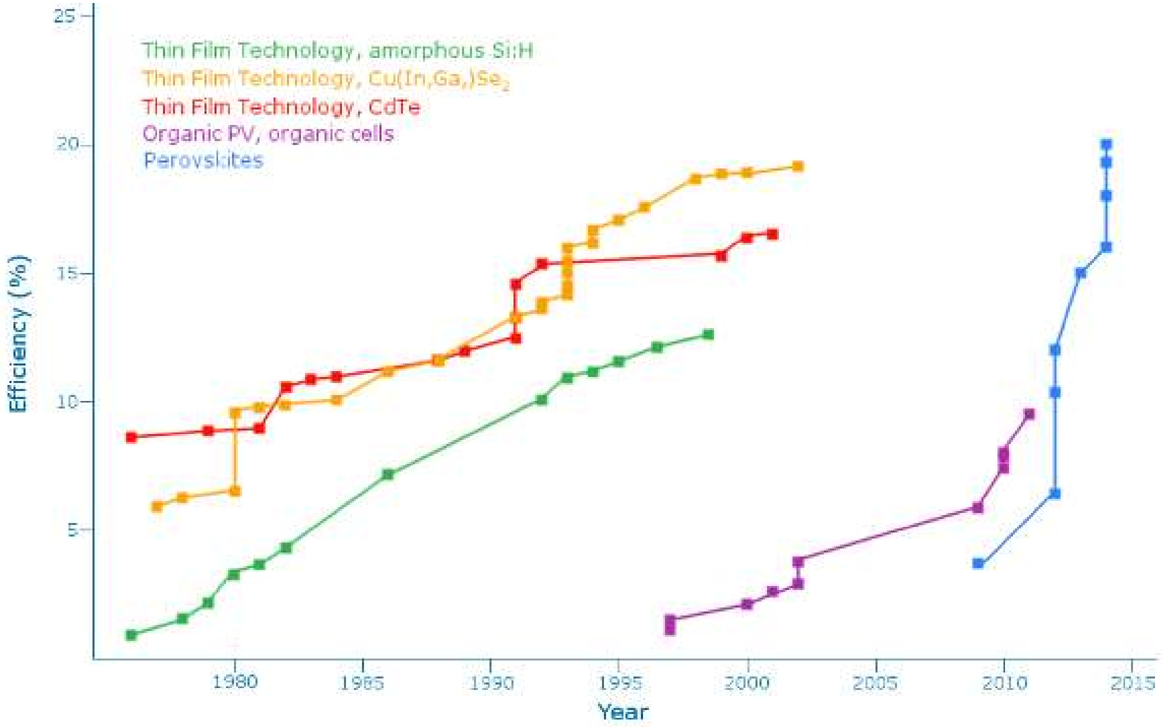
A:$Ca^{2+}$
B:$Ti^{4+}$
X:$O^{-}$

Depending on A, they can be hybrid with organic cation or fully inorganic

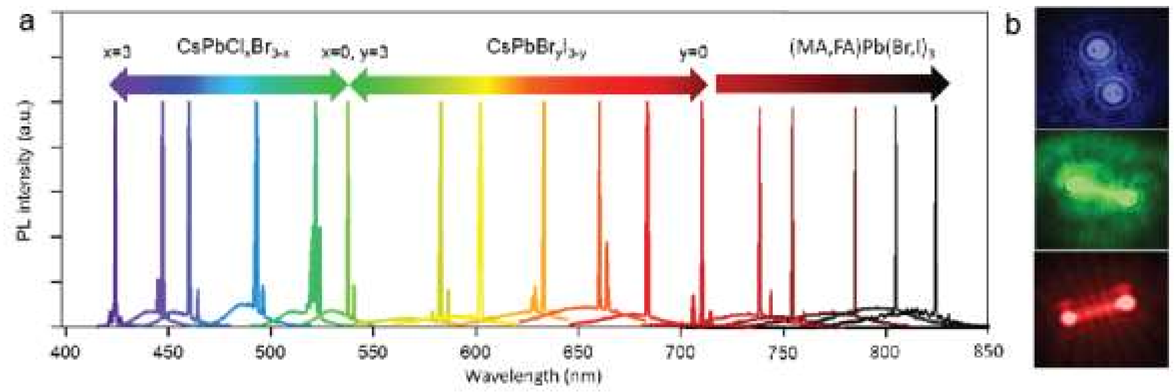
A: $CH_3NH_3$, Cs
B:Pb,Sn
X:Cl,Br,I

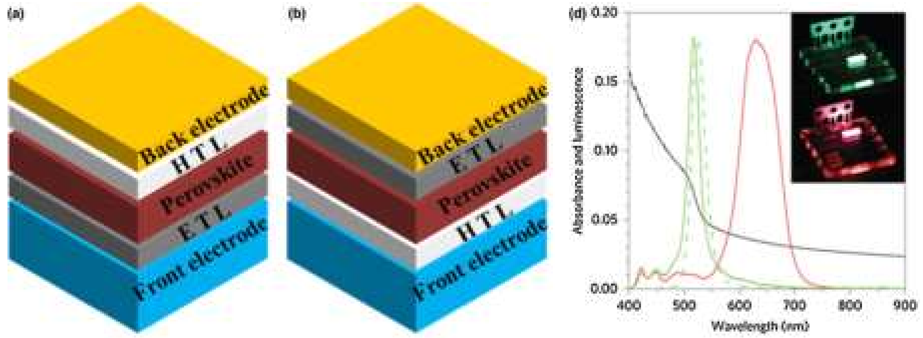
# Application Fields

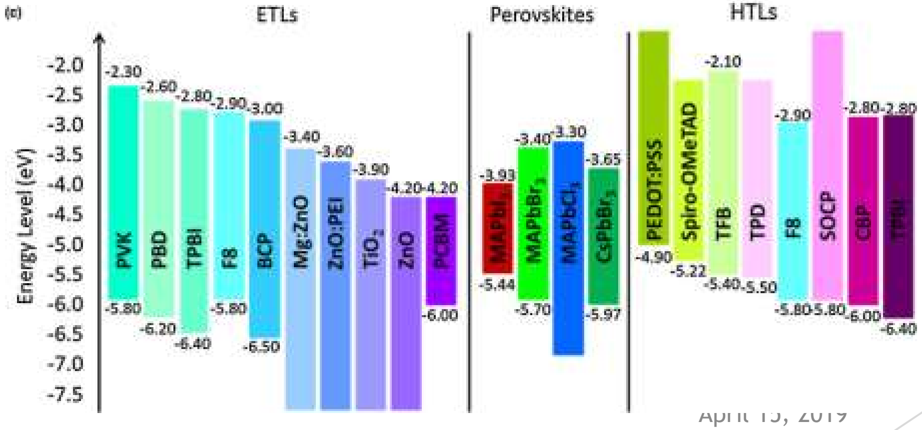
Energy Harvesting



# LEDs and Lasers



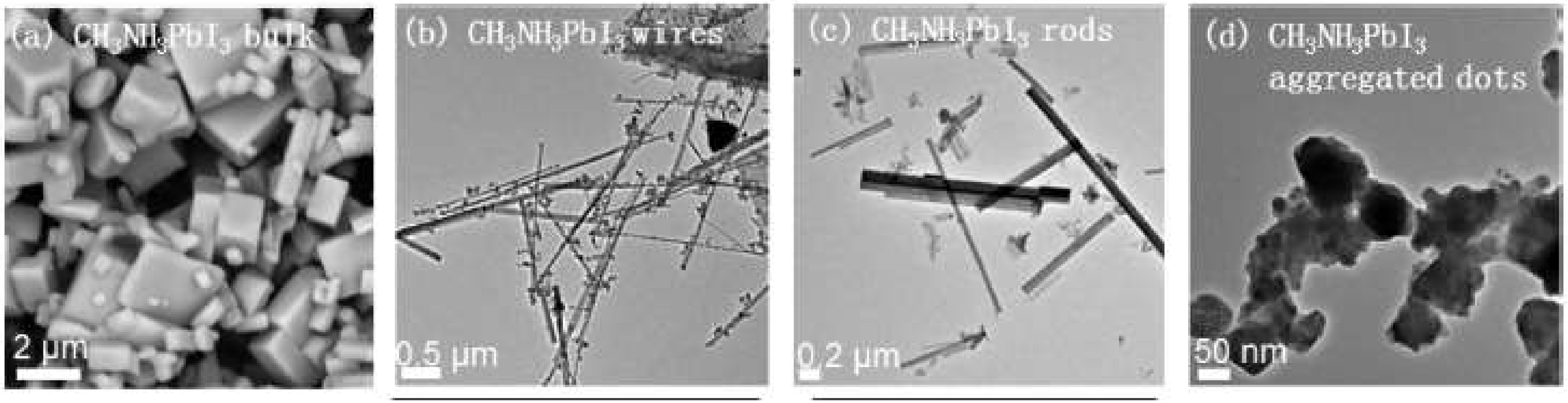






https://doi.org/10.1016/j.mattod.2017.03.021

# Different material nanostructuring means different behavior




From bulk to plates, wires, dots

# Here in Florence

- Synthesis
- Morphological  and structural characterization (XRD, SEM)
- High resolution optical spectroscopy in space and time

# Synthesis of nanostructures/thin films

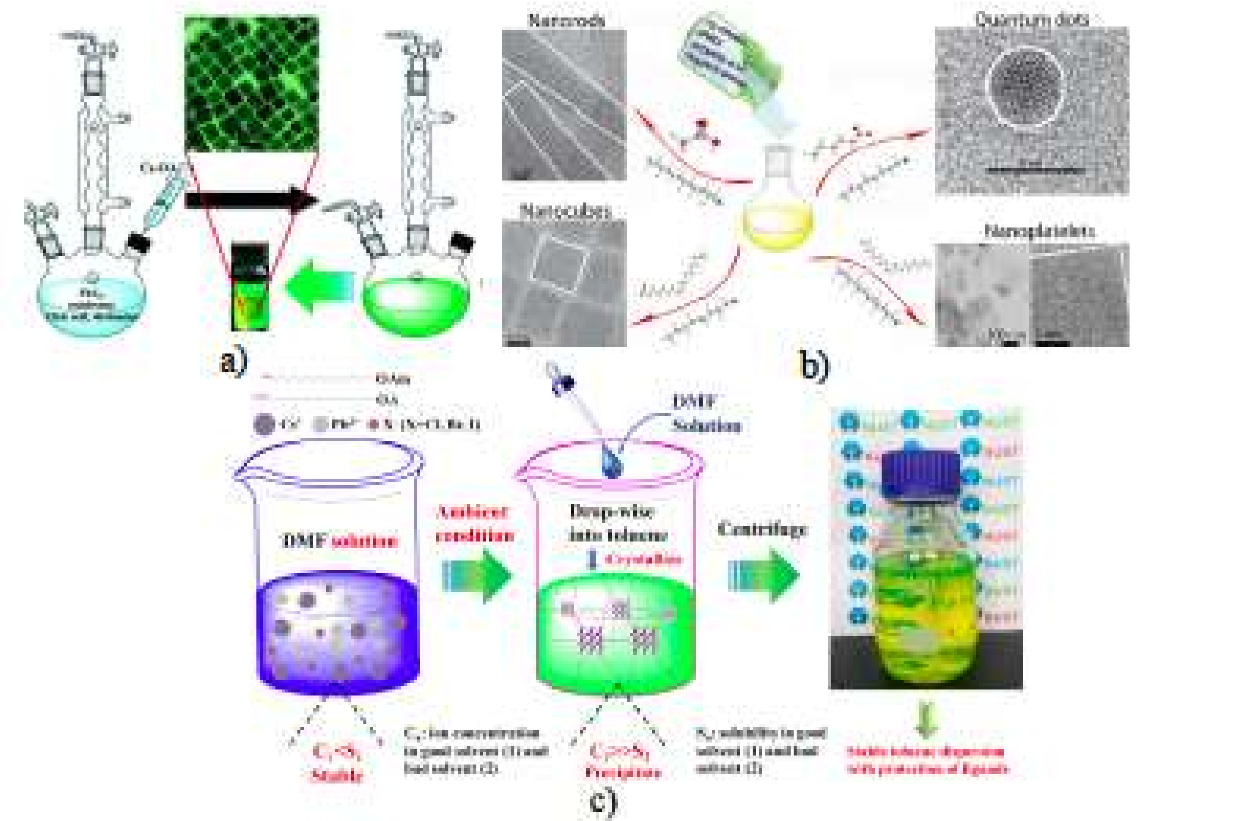
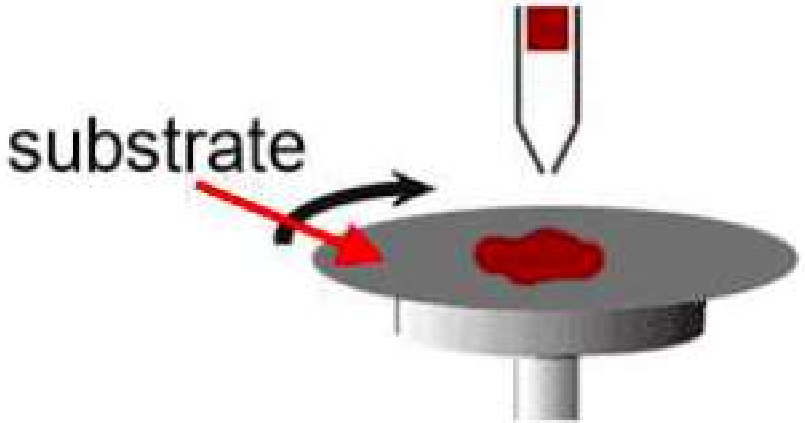



**Figure 2.4:** Schematic illustration of the most common methods to synthesize $CsPbX_3$ NCs: a) Hot injection method. The inset shows a corresponding TEM image of the as-produced NCs. b) Room temperature ligand-mediated re-precipitation. By varying the surfactants different structures can be obtained. c) Room temperature supersaturated recrystallization. [56,92,192]

# Then precursors are spin-coated on a substrate……..solvent evaporation produces perovskite



# For crystals

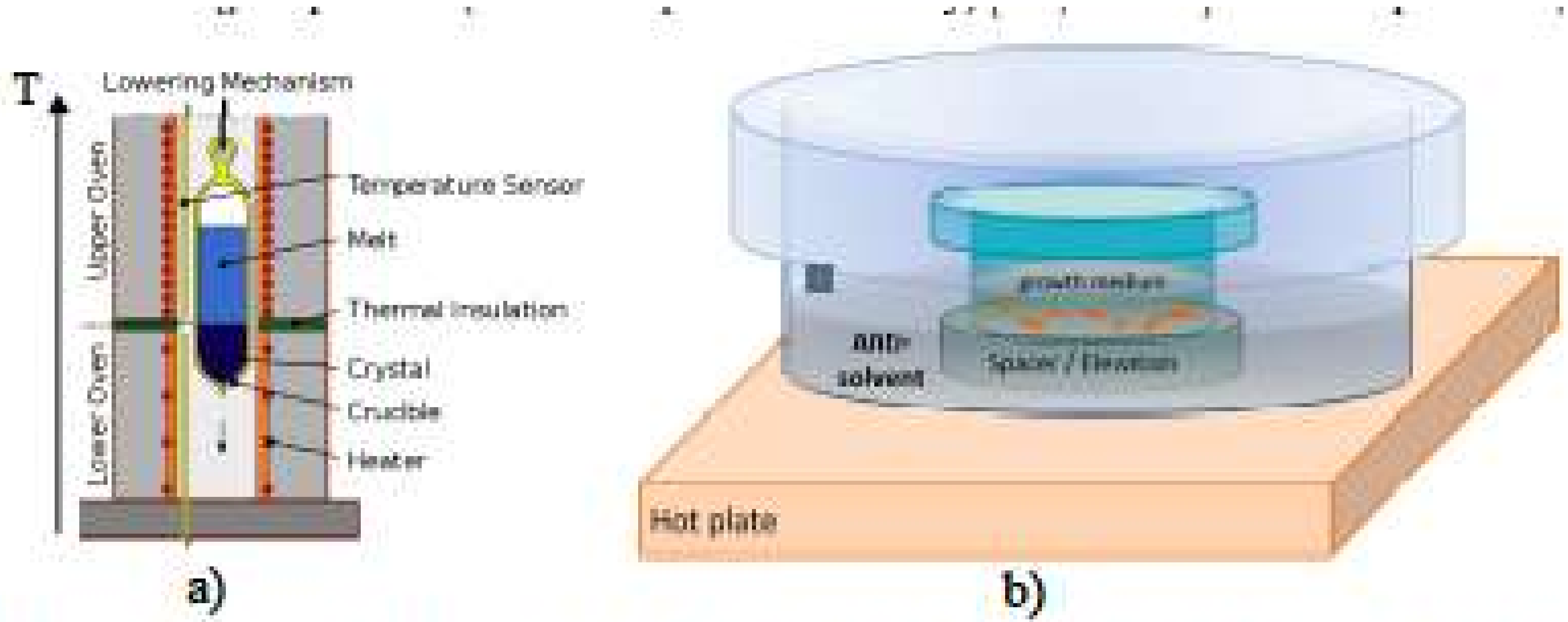
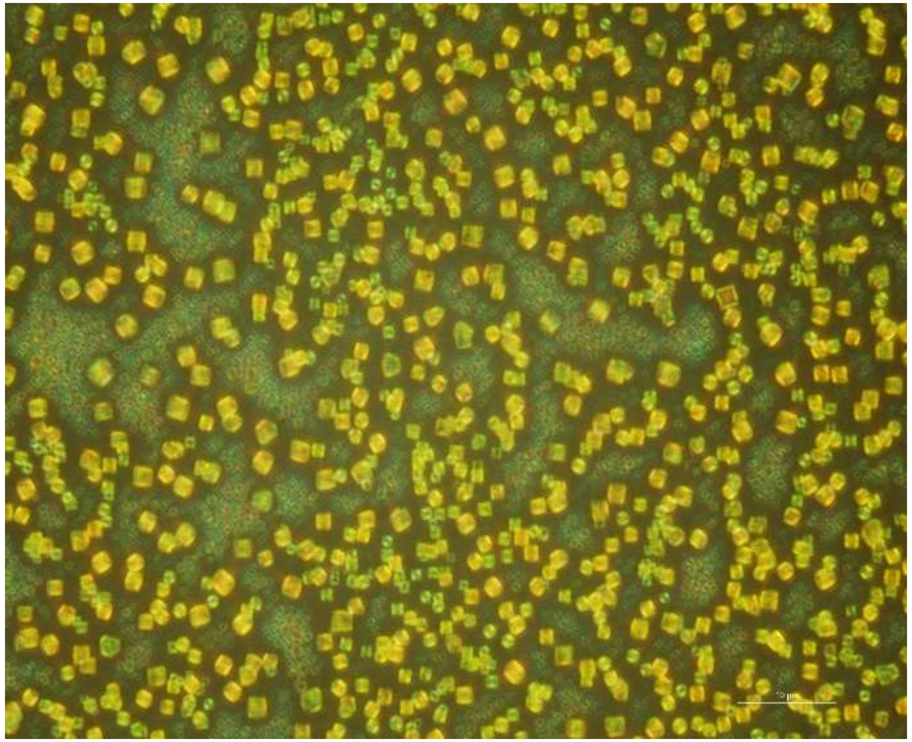
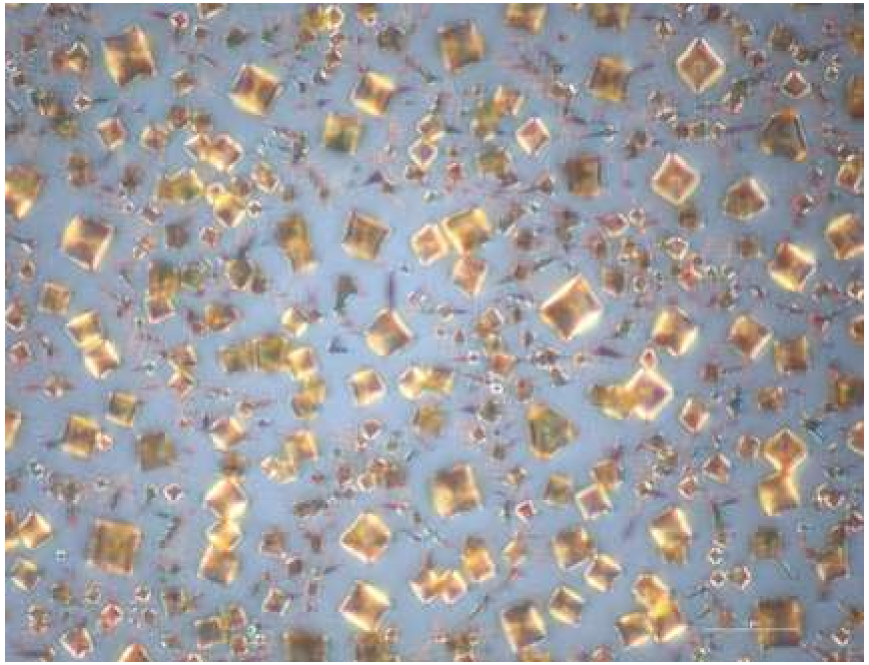



Figure 2.5: Synthesis techniques to growth perovskite single crystals: a) Bridgmann method. b) AVC method. [194]

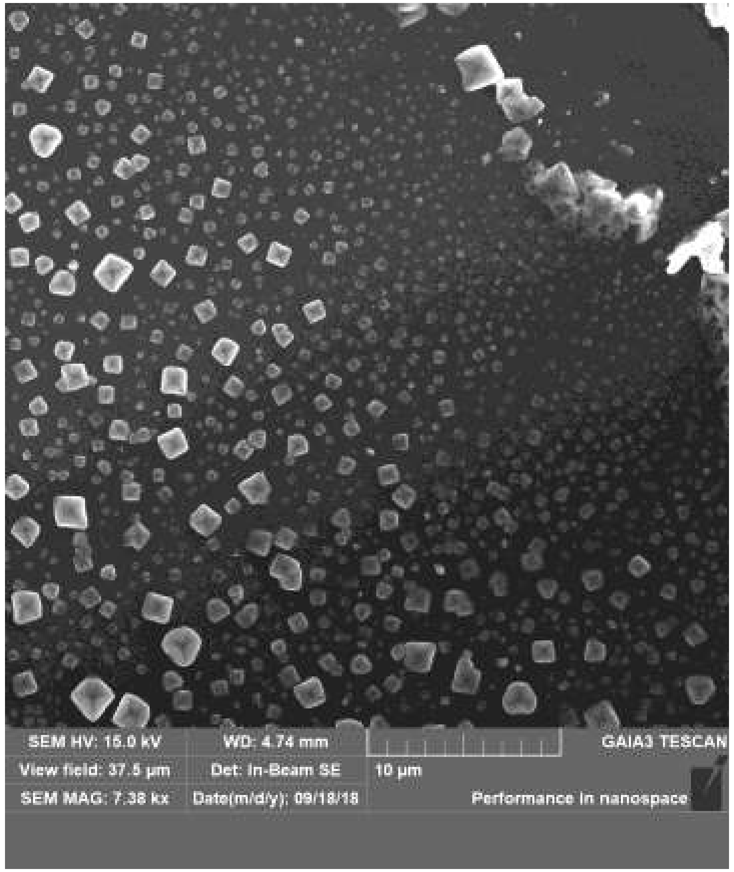
# At the optical microscope: spin-coated samples



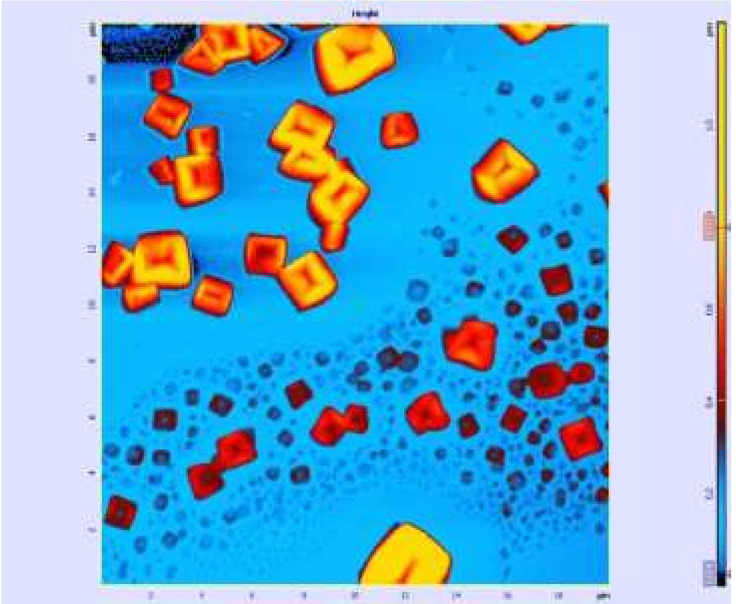


# High resolution Imaging

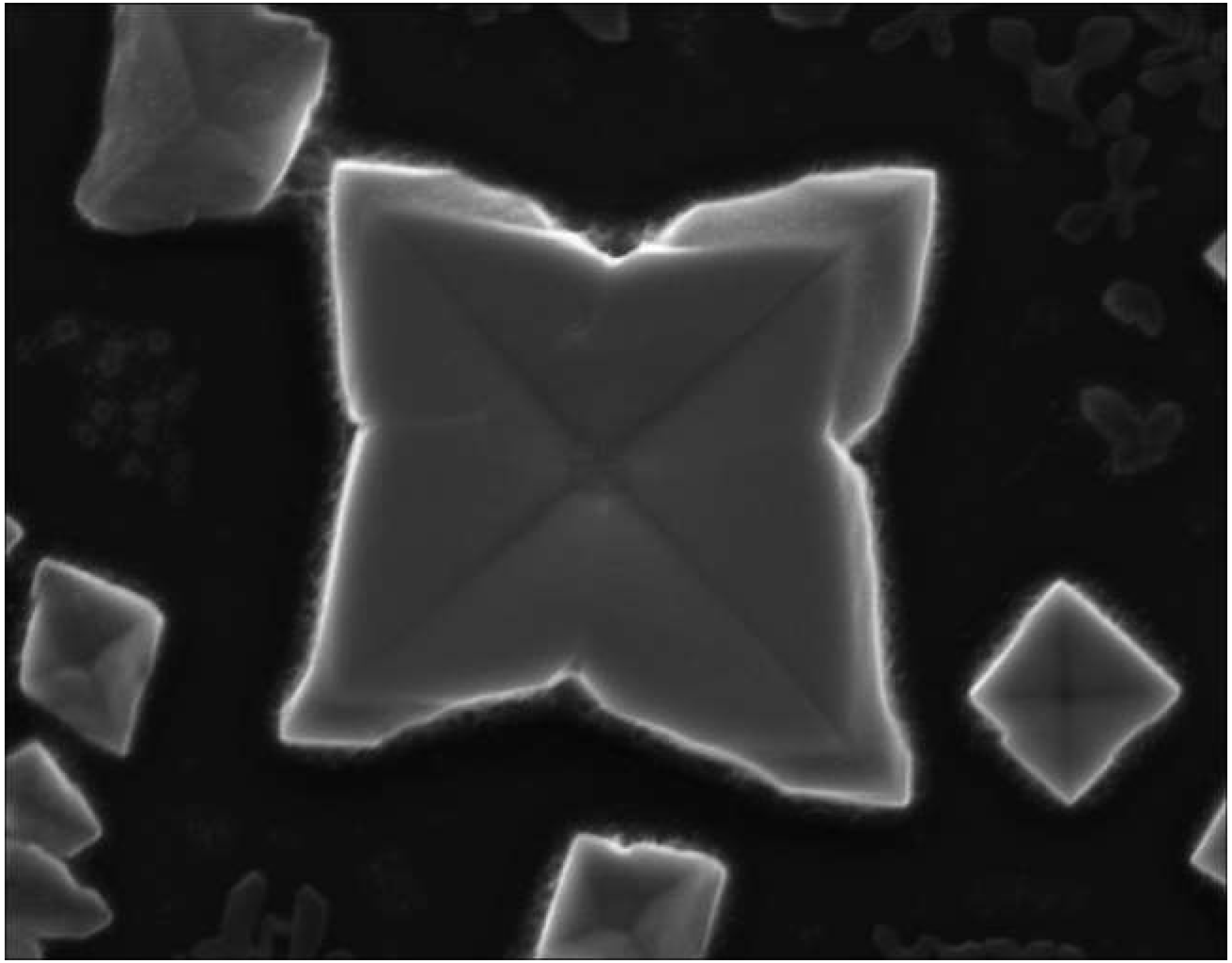
## SEM



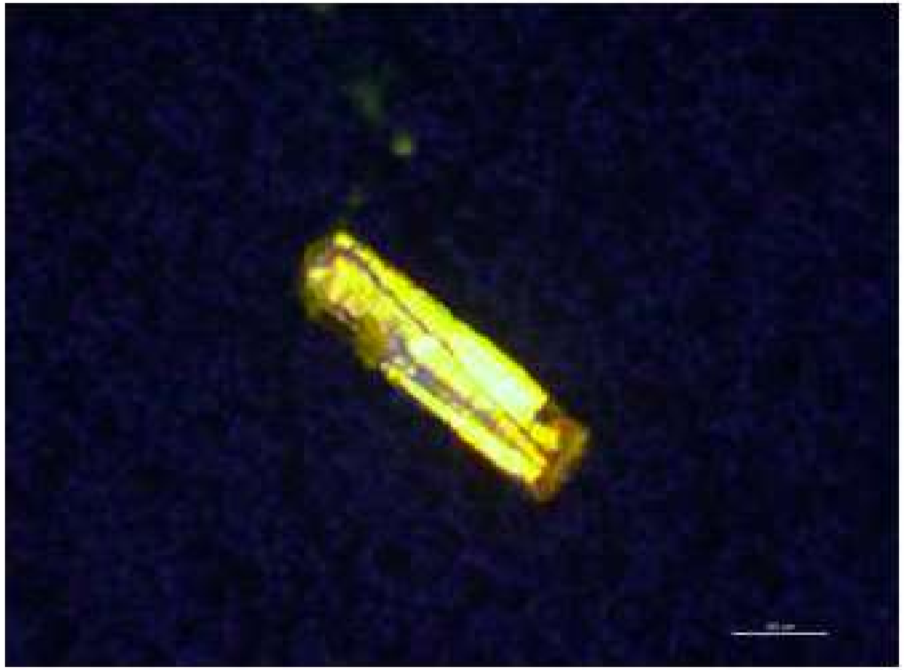

## AFM



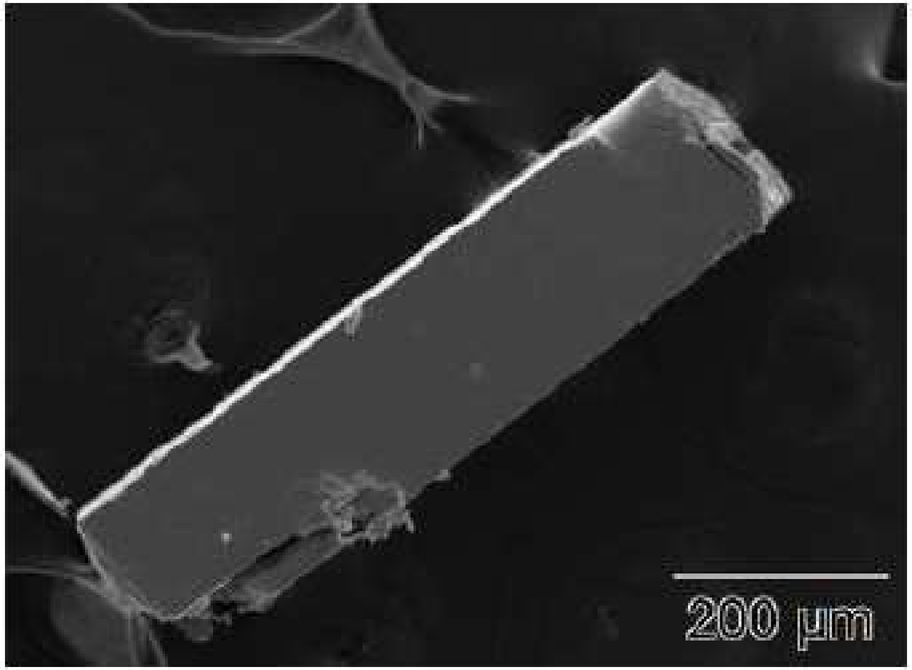
# High resolution SEM



# Bulk crystals



Using an optical microscope




Using a SEM

# What spectroscopy on such samples?

- We need to determine the bandgap: standard cw spectroscopy ( transmission/ absorption/ photoluminescence)

- We need to understand the non-radiative recombination paths: temperature-dependent measurements

- We need to understand the carrier interactions and the recombination kinetics: time-resolved experiments, typically at the picosecond time-scale

# Moreover: optical spectroscopy at the macro or micro scale?

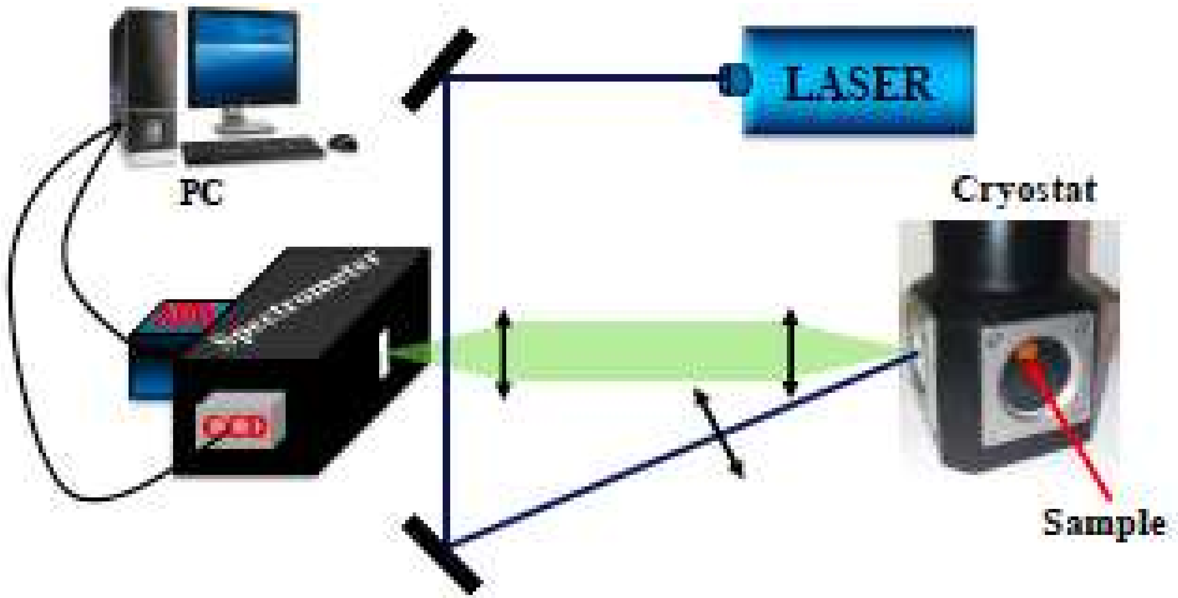
Macro: we probe macroscopic portions of the sample ( ≥ 100 μm$^2$)

Micro: Spatial resolution at the diffraction limit (≈μm in the vis)

Near Field detection: spatial resolution limited by the fiber tip ( ≈ 100 nm)

Different informations can be extracted!

# Here in the labs



# MicroPL

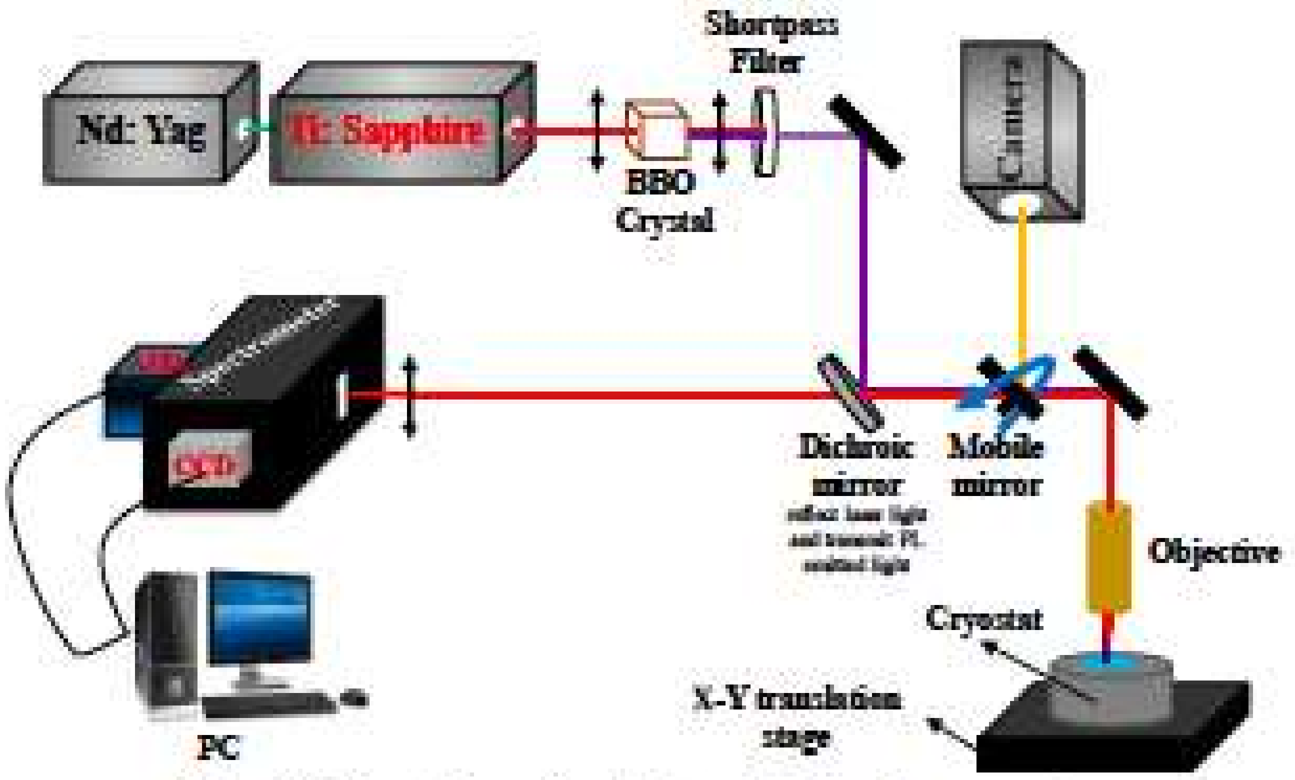
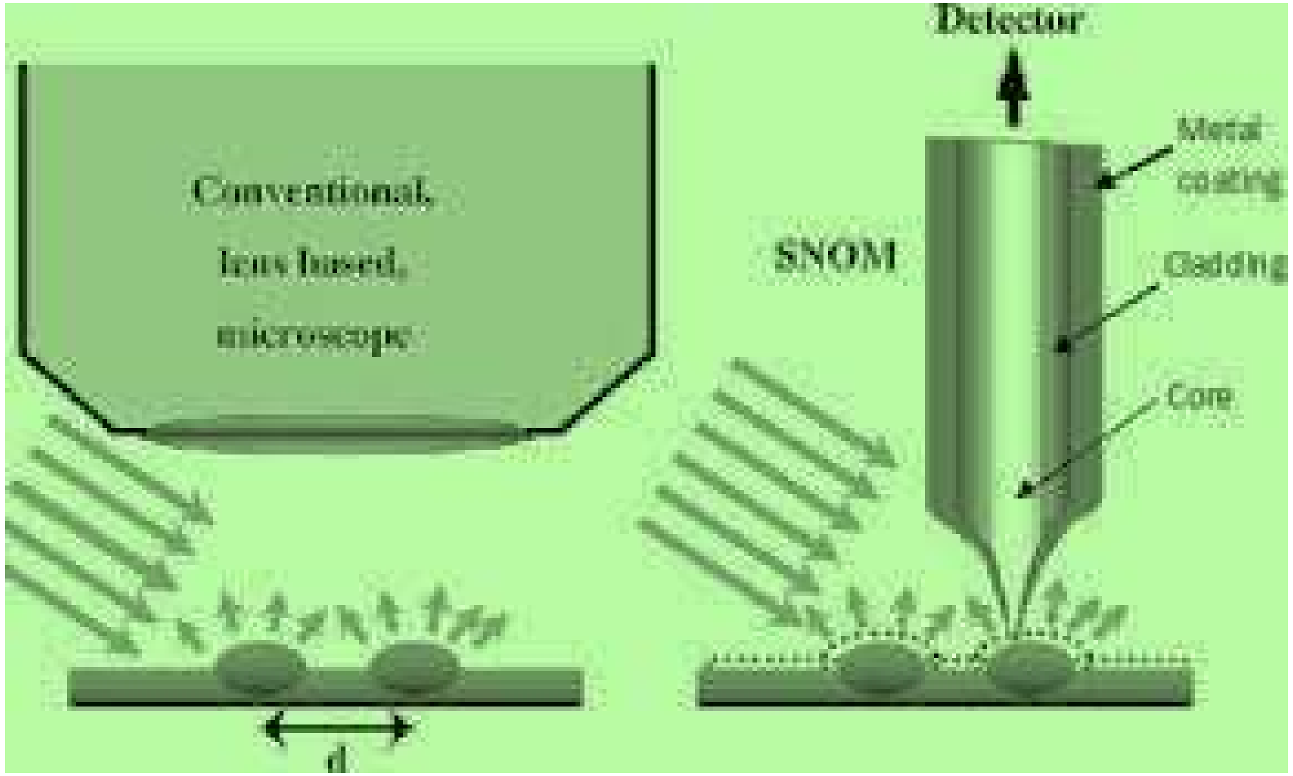
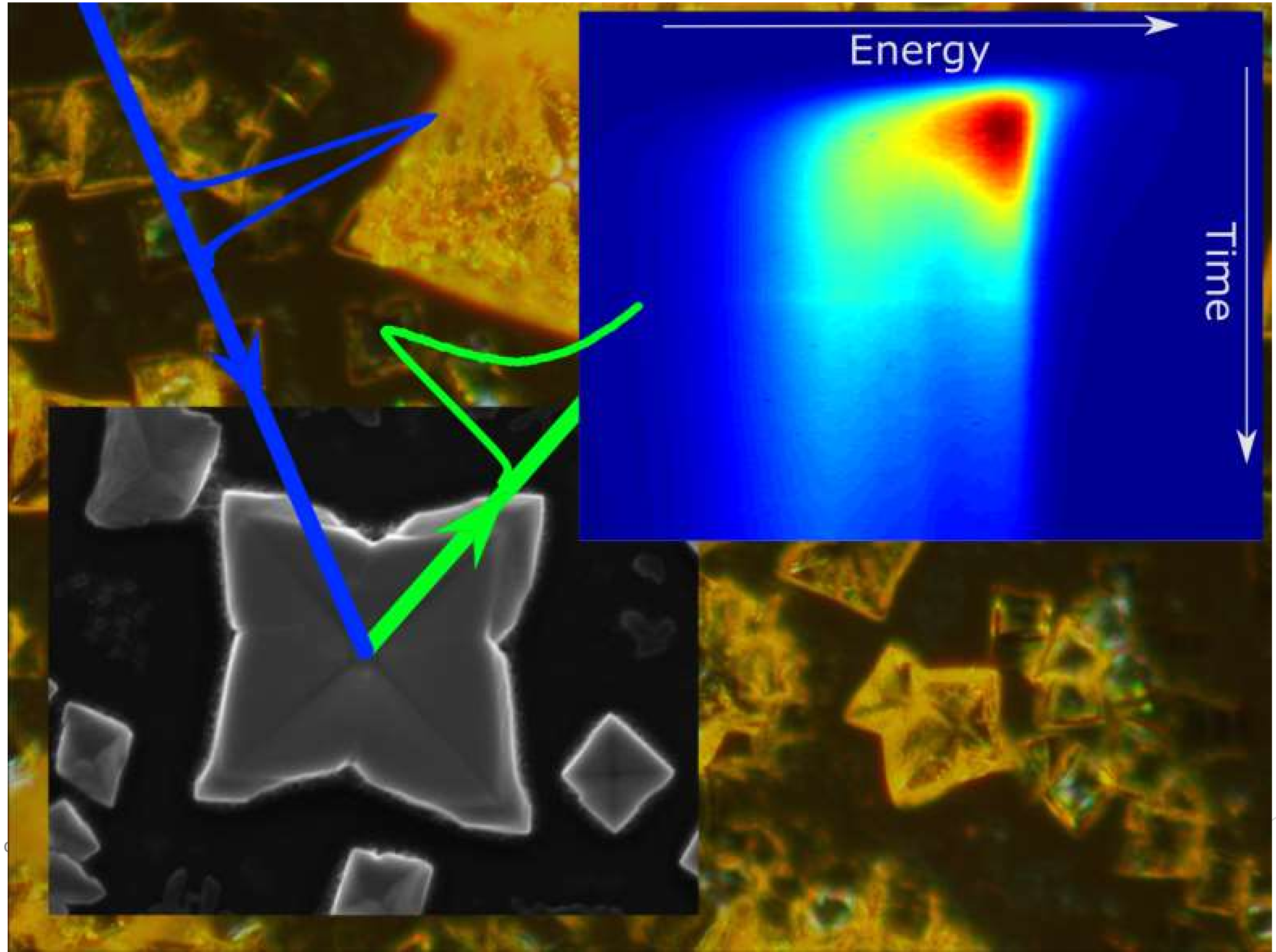



Figure 4.2: Scheme of the experimental setup used for micro-PL measurements.

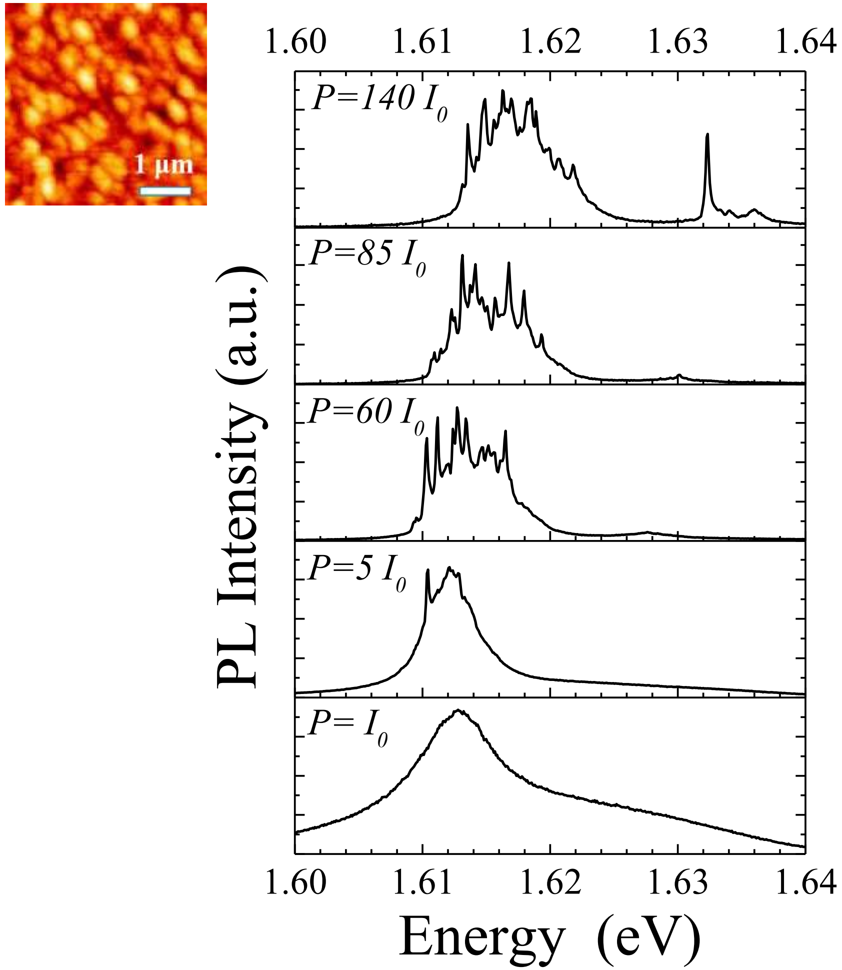
# SNOM

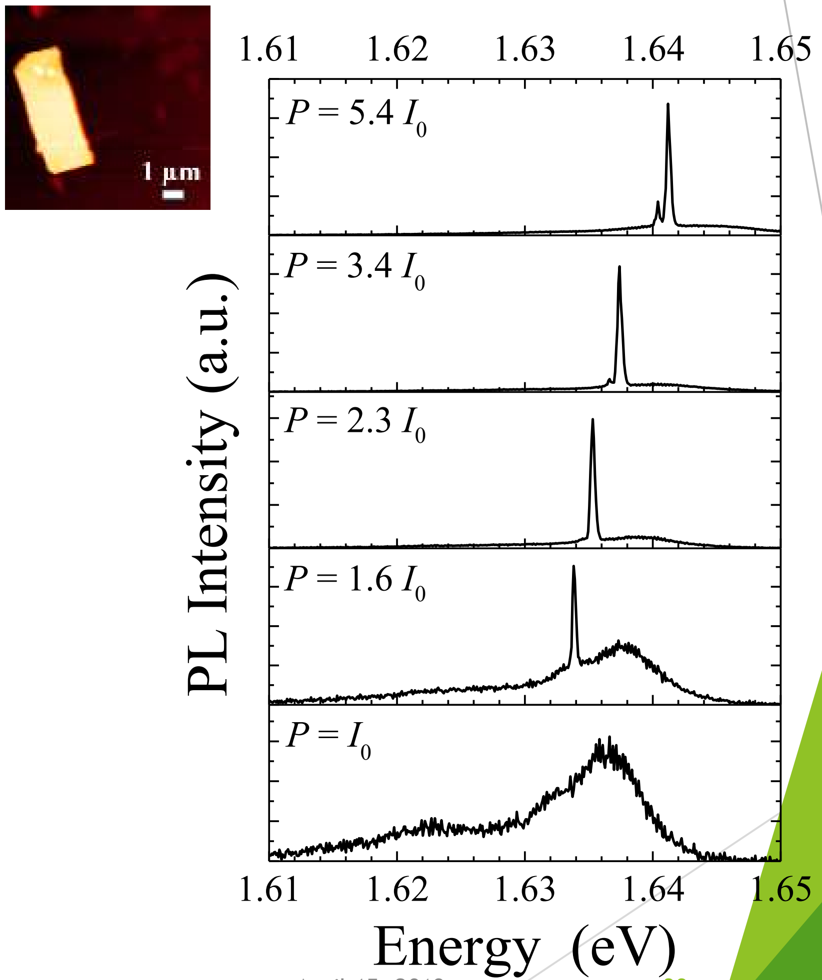

Detector
Metal coating
Conventional, lens based, microscope
SNOM
Cladding
Core
d

# At the end

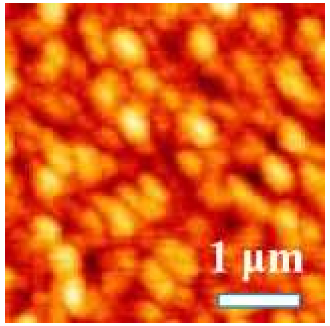


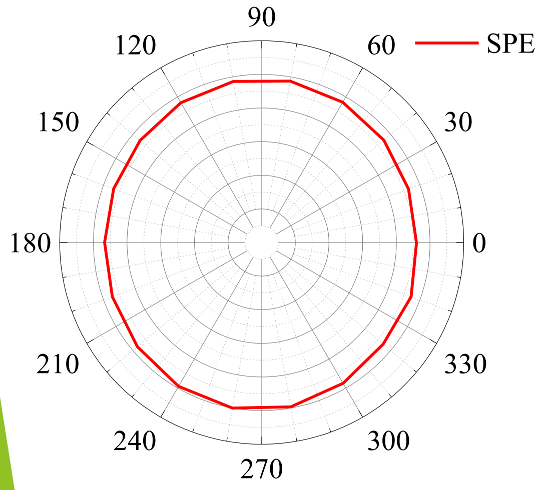
# Some examples
# Superlinear emission: ASE or lasing?

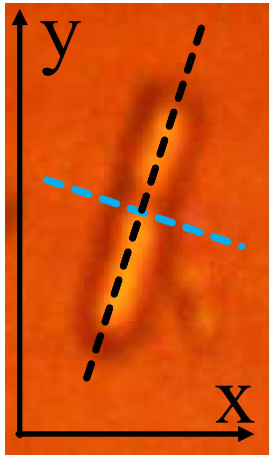


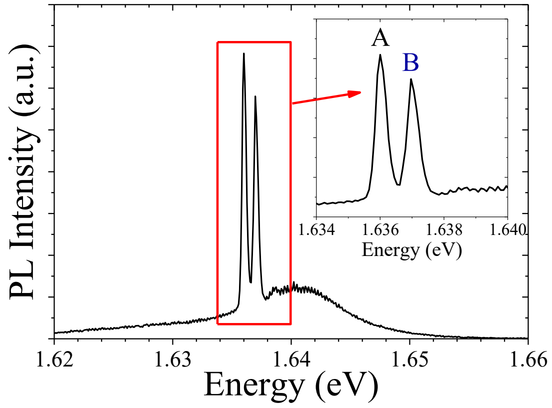



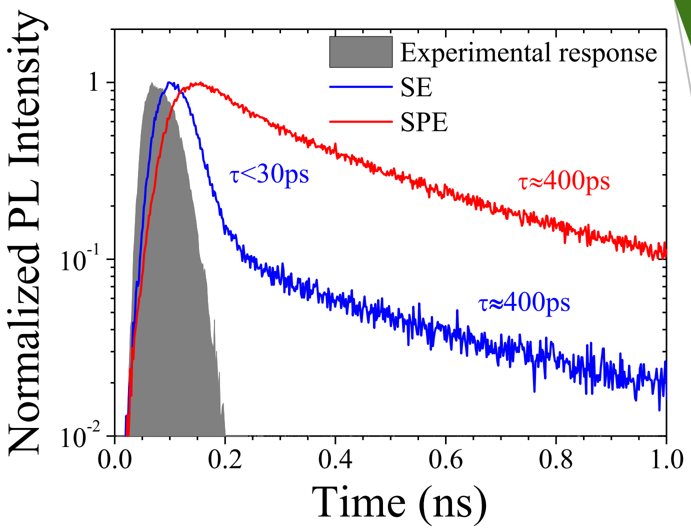
# Decay kinetics is similar but polarization properties are different

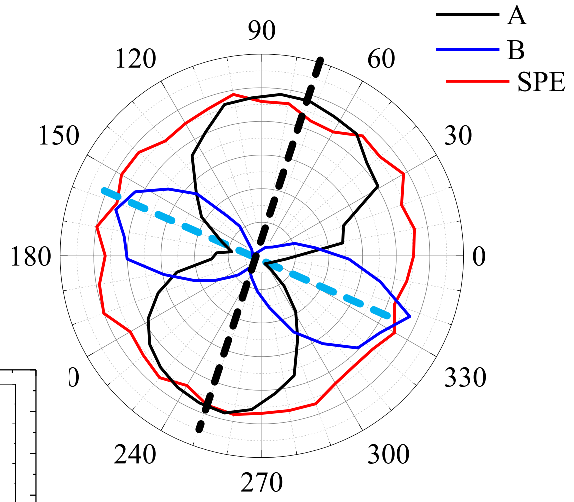


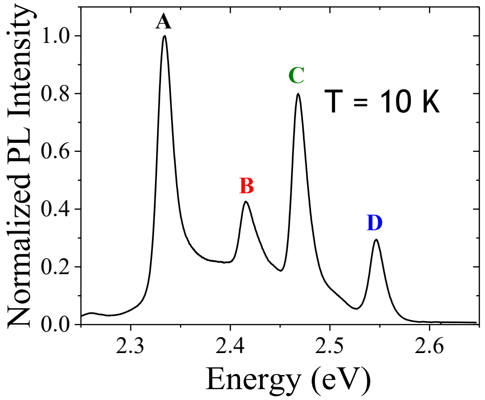



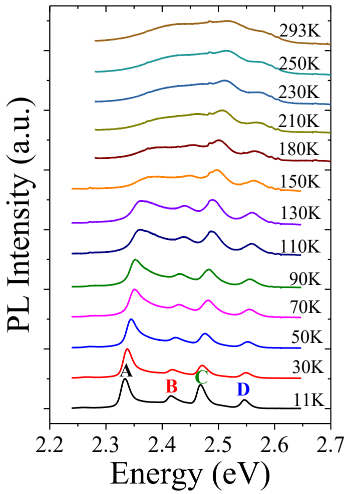



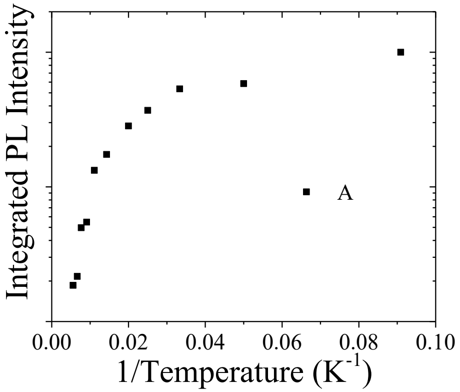



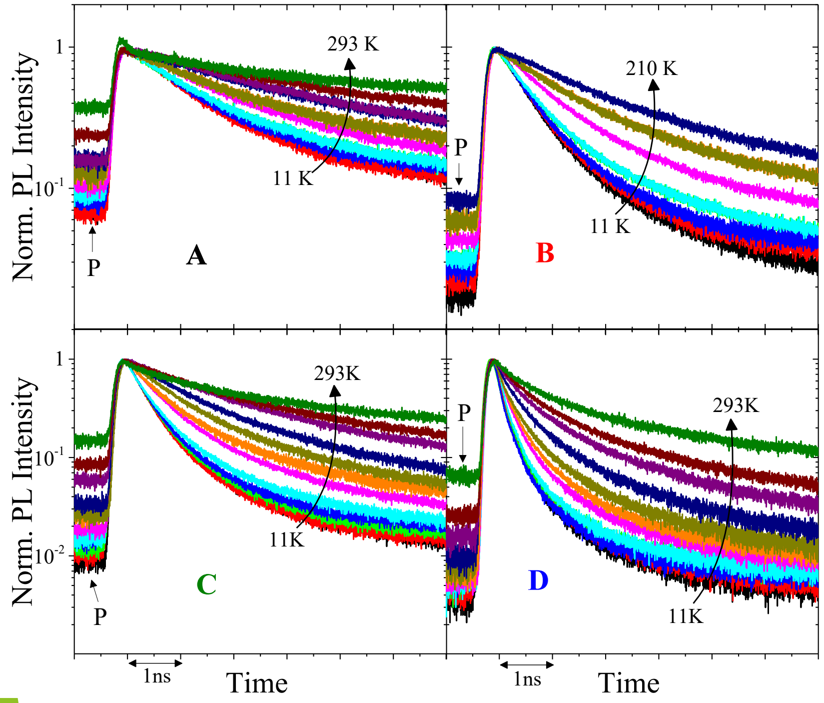



# Surface states role



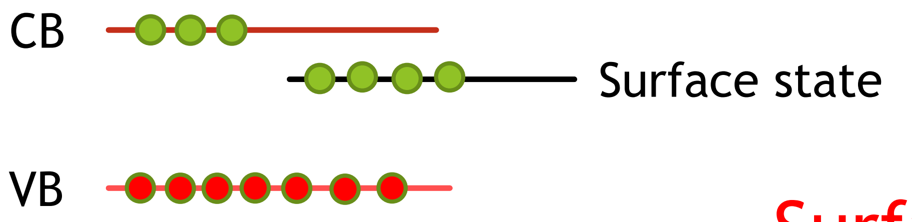

**Recombination dynamics slows down increasing the temperature!**

**The smaller the nanocrystals, the larger the effect**

## The increase of lifetime with T is counterintuitive ! Usually non radiative channels are more effective as T increases But….

Large crystals or high temperature (smaller barrier, less surface defects)

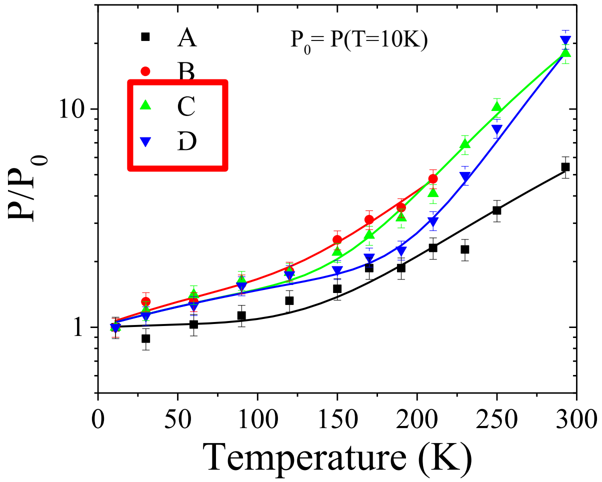
Small crystals or low temperature (larger barrier, more surface defects)




Surface states act as a reservoir an can release population as T increases

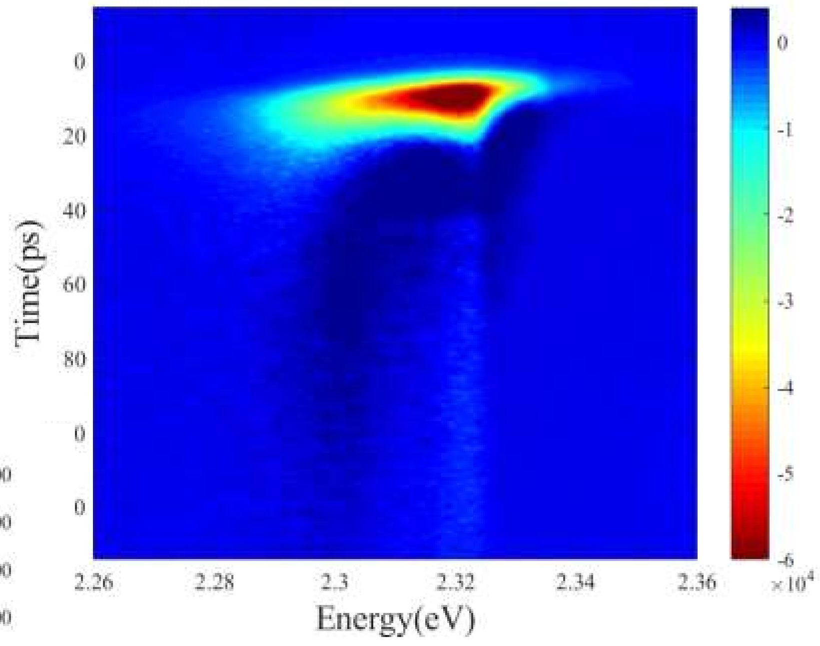
# Thermally activated transfer

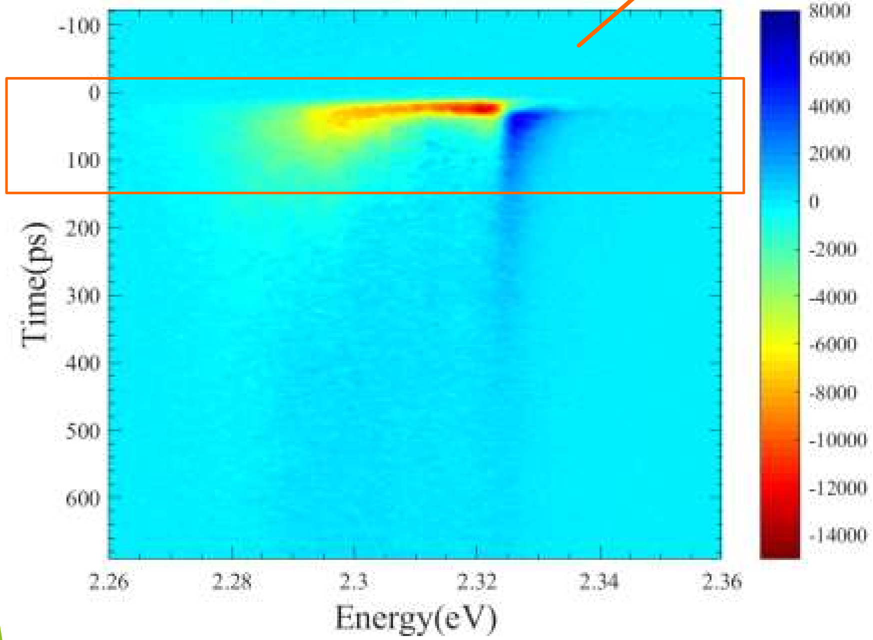
$$P(T) = AT + Be^{-\frac{E_B}{k_B T}}$$




| Band | A ($K^{-1}$) | B ($10^{-3}K^{-2}$) | $E_B$ (meV) |
|---|---|---|---|
| A | ≈ $10^{-3}$ | 0.18 | 33 |
| B | | 0.48 | 39 |
| C | | 2.6 | 67 |
| D | | 25 | 130 |

# Non-linearities with two beams



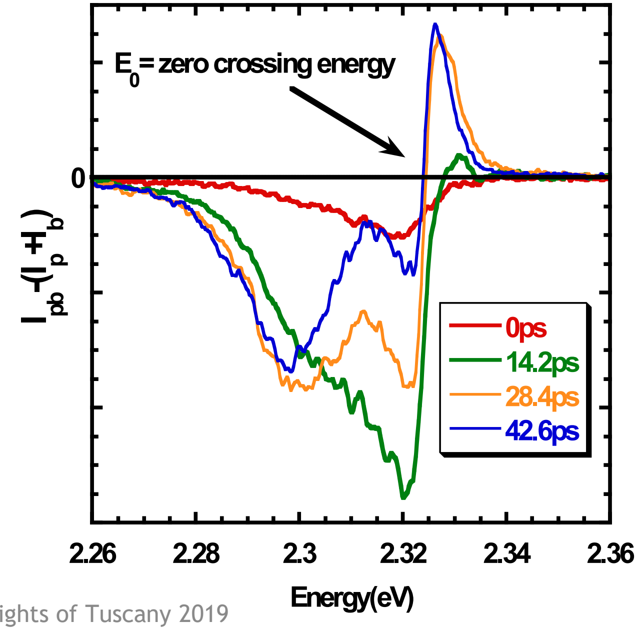

Non resonant bias CW @ 405 nm + ps pulse @ 370 nm

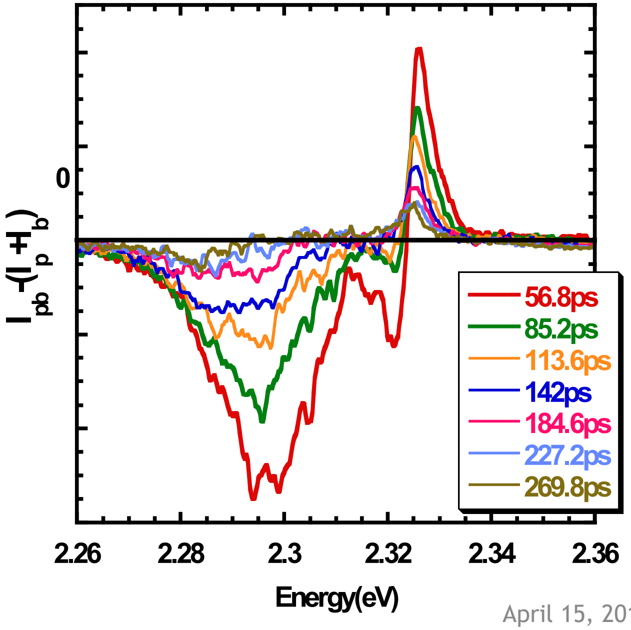
$I_{pb}$- ($I_p$+$I_b$) vs time

nanop2018-Rome October 1-3

44

# Negative signal: bleaching related to localized/bound states
# Positive signal: Superlinearity from excitons formation



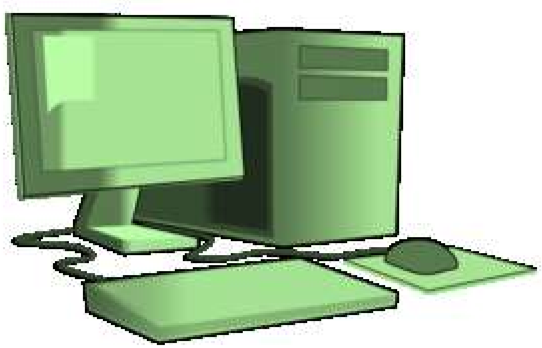
# Conclusions

Optical spectroscopy implemented in several different configurations allows to provide a dramatic amount of physical information which is fundamental for the progress of material science.
New classes of artificial-made materials recently realized are of relevance for opto devices: in these years perovskites are probably the most investigated !

# A look to the future

- Controlled deposition of nanocrystals and homogeneous film
- Definition of post-growth treatment for defect annealing
- Coupling of perovskites to photonic structures to tailor the light properties
- Optimization of electrical injection for realization of Leds and Lasers
- Eco-friendly materials ( no lead, etc)

# Let’s try to think our lives without semiconductors: just 3 objects



# Could you survive?

Thanks