Scuola Superiore ISUFI
Nanoscience Grid-Computing Section

Università del Salento

Nanostrutture a confinamento quantistico elettronico: i quantum dot

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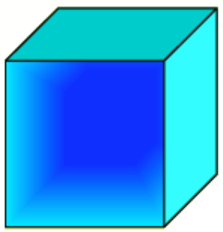
NNL National Nanotechnology Laboratory of I.N.F.M.

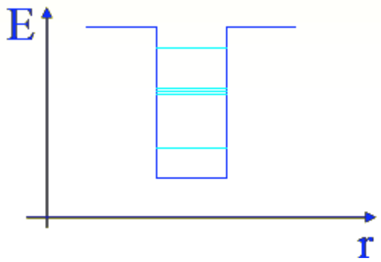
Outline

- Properties of quantum dots (QDs)
- Synthesis of quantum dots
  - *Self organized epitaxial quantum dots*
  - *Colloidal quantum dots*
- Device and applications of different types of quantum dots
- Conclusions

What is a quantum dot

- A confining potential in three dimensions whose size has no sharp definitions
- Wave nature of carriers is important
 (of the order De Broglie wavelength ~ 10 nm in InAs)
- Discrete states (Artificial atoms)
- Quasi zero-dimensional systems

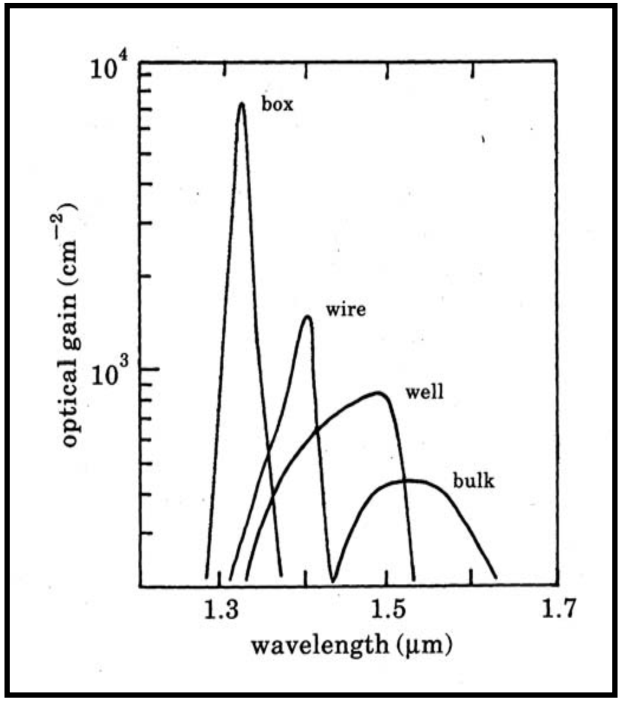




The ideal QDs

- Precise size and shape (box or sphere) with uniform composition
- Infinite quantum confinement
- Array of identical quantum dot
- For a cubic dot (size L):

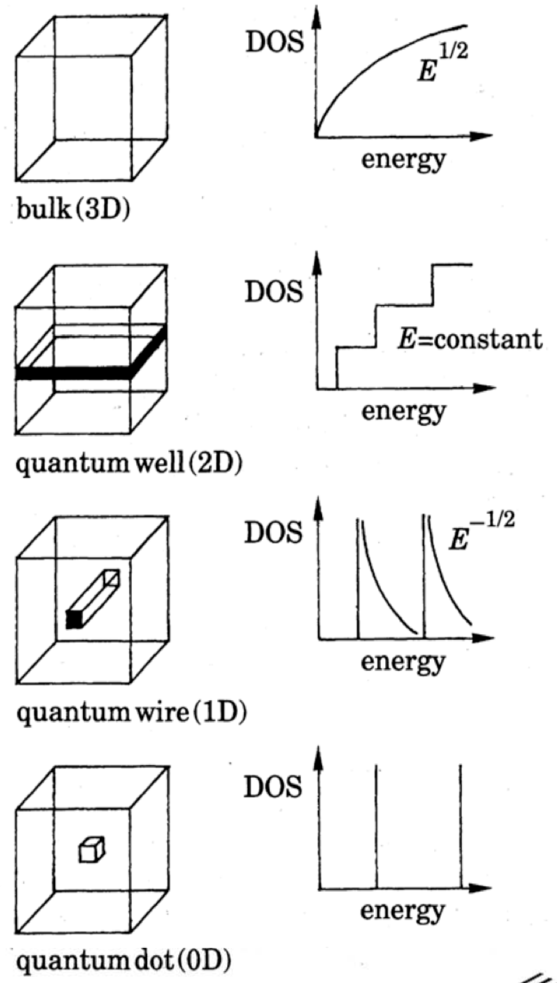
$$E_{n_1 n_2 n_3} = E_g + \frac{\hbar^2 \pi^2}{2 m_r L^2}\left(n_1^2 + n_2^2 + n_3^2\right), \quad n_i = 1, 2, 3$$



Asada et al., JQE (1986)

Properties of quantum dots

- Delta Function DOS
- Ground state above Bandgap
- Less active states than a bulk device of the same size
- High material gain
- Narrow and symmetrical gain
- Low optical density
- Gain saturation
- Difficult technology



Applications of epitaxial QDs

- Improve existing devices:
  - Lasers and MCLEDs
  - Optical amplifiers
  - Long Wavelength detectors
- Novel devices and applications
  - Spintronics
  - Quantum computing
  - Quantum cryptography (single photon emitters)
  - Optical memories
- Unique physics compared to bulk semiconductors materials

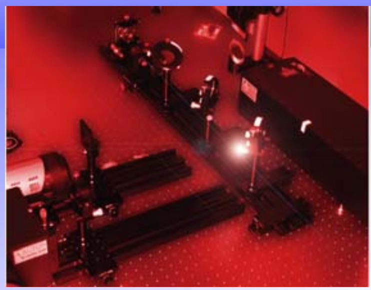
SEMICONDUCTOR QUANTUM DOTS BASED PHOTONIC DEVICES

Telecommunications and information technology demand fast and reliable data exchange on wide-world area networks

Development of optical data transmission systems requiring:

- low-cost
- 1.3 μm emitting
- spectrally pure
- low-power operating
- temperature insensitive
- fast modulating

LASER SOURCES



Display and Lightning technology looking for bright, high-resolution, multi-color or white emitting light sources

Development of:

- cheap
- spectrally tunable
- long-lasting
- bright
- controlled at micron-scale

LIGHT SOURCES

Pioneering studies on quantum cryptography and **non-classical photon sources**

Development of:

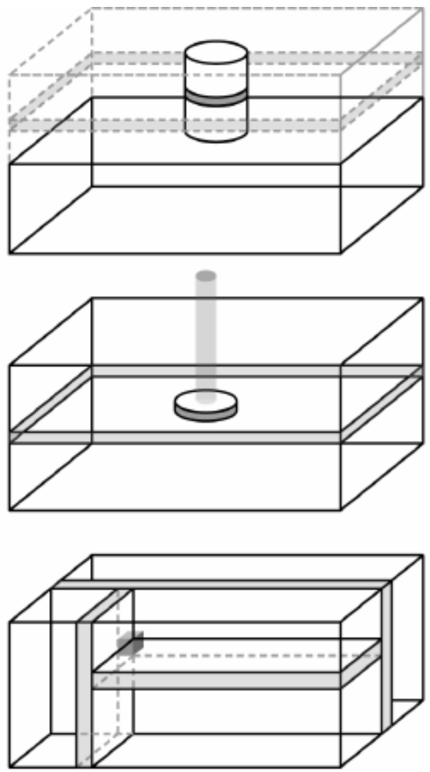
- reliable
- spectrally ultra-pure
- long-lasting
- room-temperature working

PHOTON SOURCES

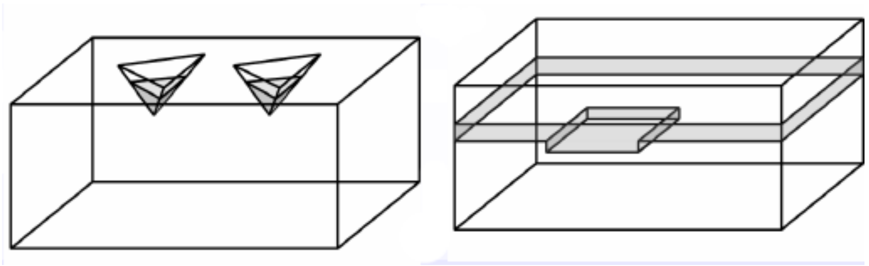
Synthesis of QDs

- Top-down approach
- Self-organization: Stranski Krastanov epitaxial growth
- Colloidal quantum dots

Top-down approach for QDs



- slow process, difficult to have large amount of QDs
- Uniform QDs (limit by litography)
- Defect states at interfaces due to etching

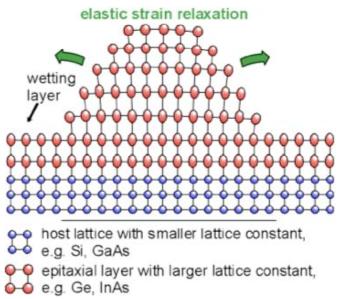


Bottom-up synthesis of QDs

- Colloidal quantum dots
- Stranski Krastanov epitaxial growth

Bottom-up synthesis of QDs

Epitaxial QDs



✓ Stranski-Krastanow growth

× Growth facilities: Metal-Organic Chemical Vapor Deposition (**MOCVD**) /Molecular Beam Epitaxy (**MBE**)

× pyramidal-shaped or lens-shaped islands; **lateral size ~ 10–40 nm** and **heights ~5–8 nm**

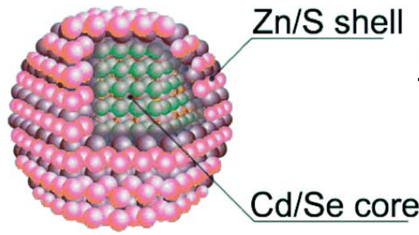
× **room-temperature emission** from single QD **difficult** to be achieved due to phonons energy comparable with allowed energy levels distance

✓**complete burying of QDs into solid crystalline matrix**: low surface defects, high photostability, high radiative recombination rates

✓ **efficient electrical injection** by p-n doping of the surrounding heterostructure

× size fluctuation in QD layers: **inhomogeneous broadening**

Colloidal QDs



✓ Wet-chemical synthesis

✓ Growth facilities: Schlenk line, liquid solution / **Low-cost** and **high throughput** fabrication method

✓ spherical shape with **diameter ~ 2-6 nm**

✓ higher distance among allowed energy states in conduction and valence bands: intense emission also at **room temperature**

× lack of a solid matrix: **spectral shifting** and **blinking** of the single emitter / Need to insert QDs from liquid solution to solid matrices

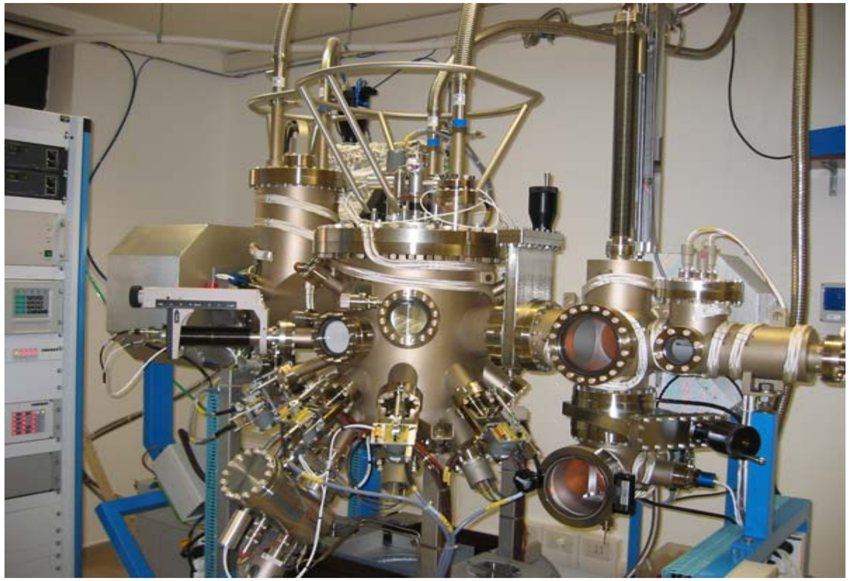
× easy optical pumping / **not straightforward electrical pumping**

× **inhomogeneous broadening**

Epitaxial growth techniques: MOCVD e MBE

Differences:

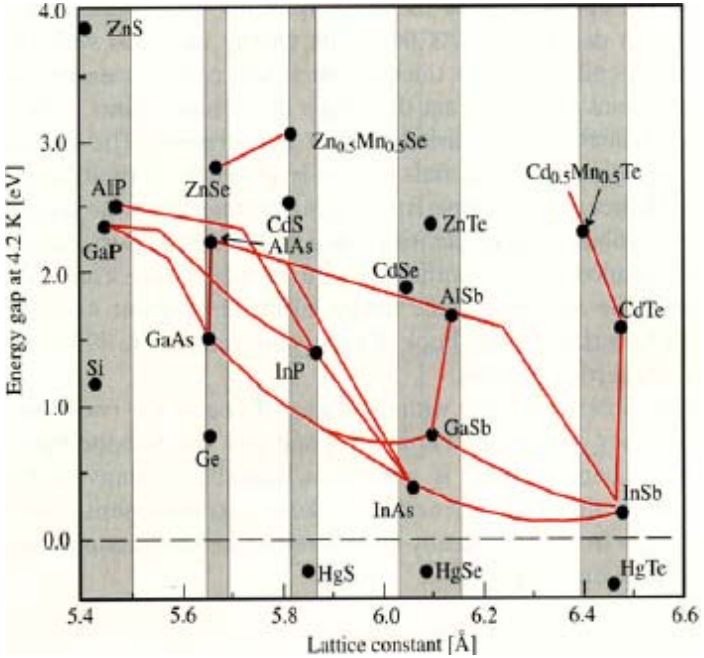
- Growth rate
- UHV and situ monitoring
- safety and materials



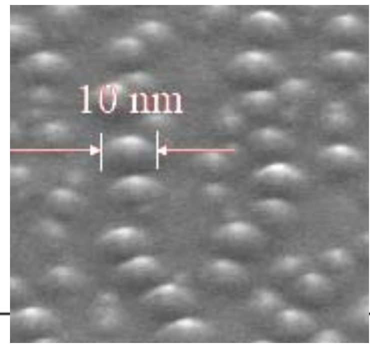
Self assembled QDs

Epitaxial growth: Interplay of surface energy and strain

"Standard" (Frank-van der Merve) 2D epitaxial growth:

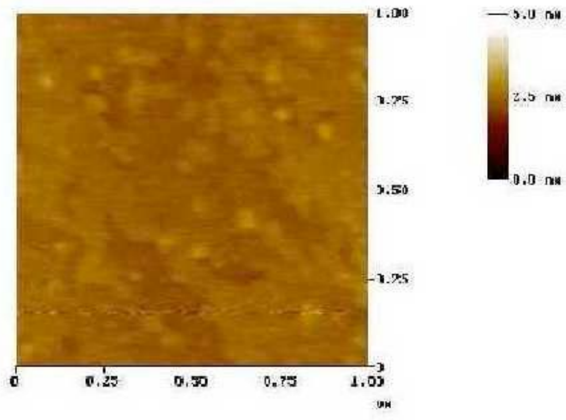


Stranski-Krastanov 3D growth mode (strain-driven):

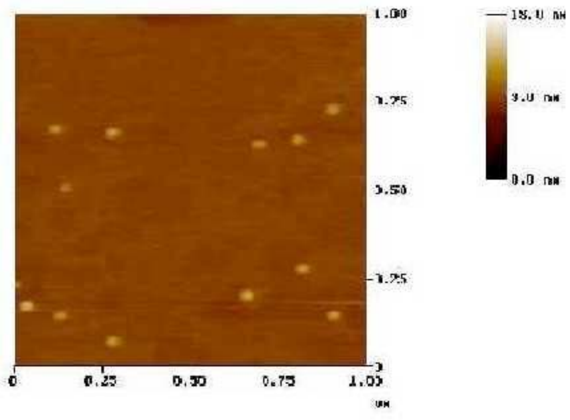


MOCVD QDs

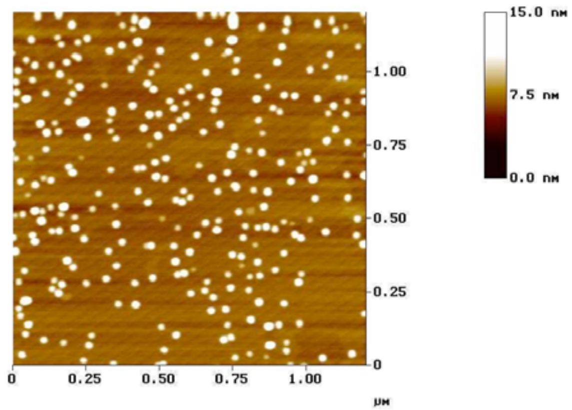
EFFECT OF THE GROWTH RATE



G.R.=0.4 ML/s



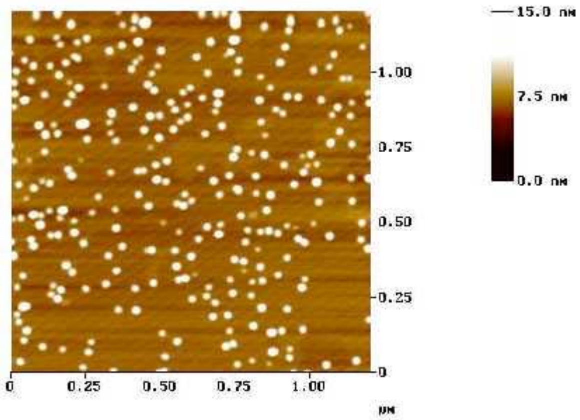
G.R.=1 ML/s
r ≈ 17 nm



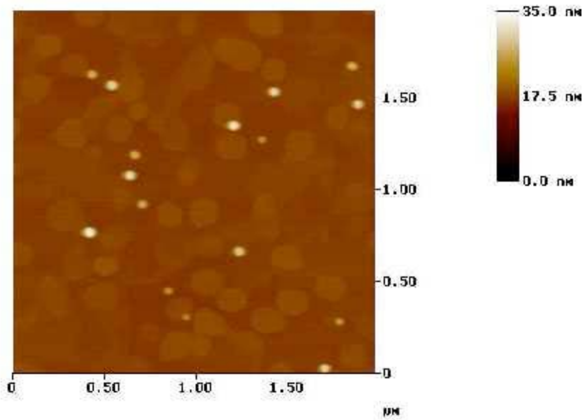
G.R.=2 ML/s
r ≈ 11 nm

6ML QDs, T=550 °C

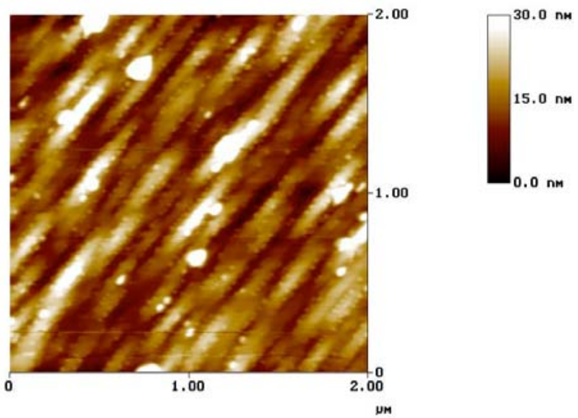
Effect of the Growth Temperature



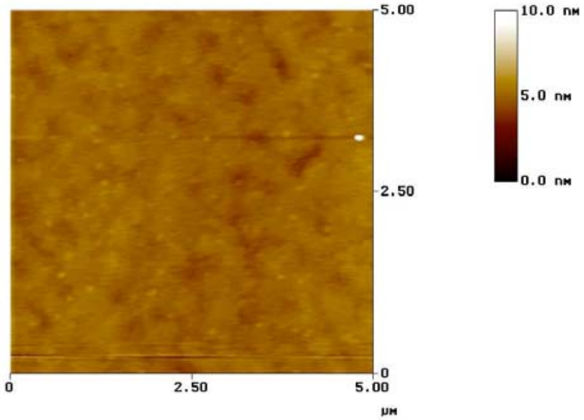
T=550 °C – Gr=2 ML/s



T=600 °C – Gr=2 ML/s



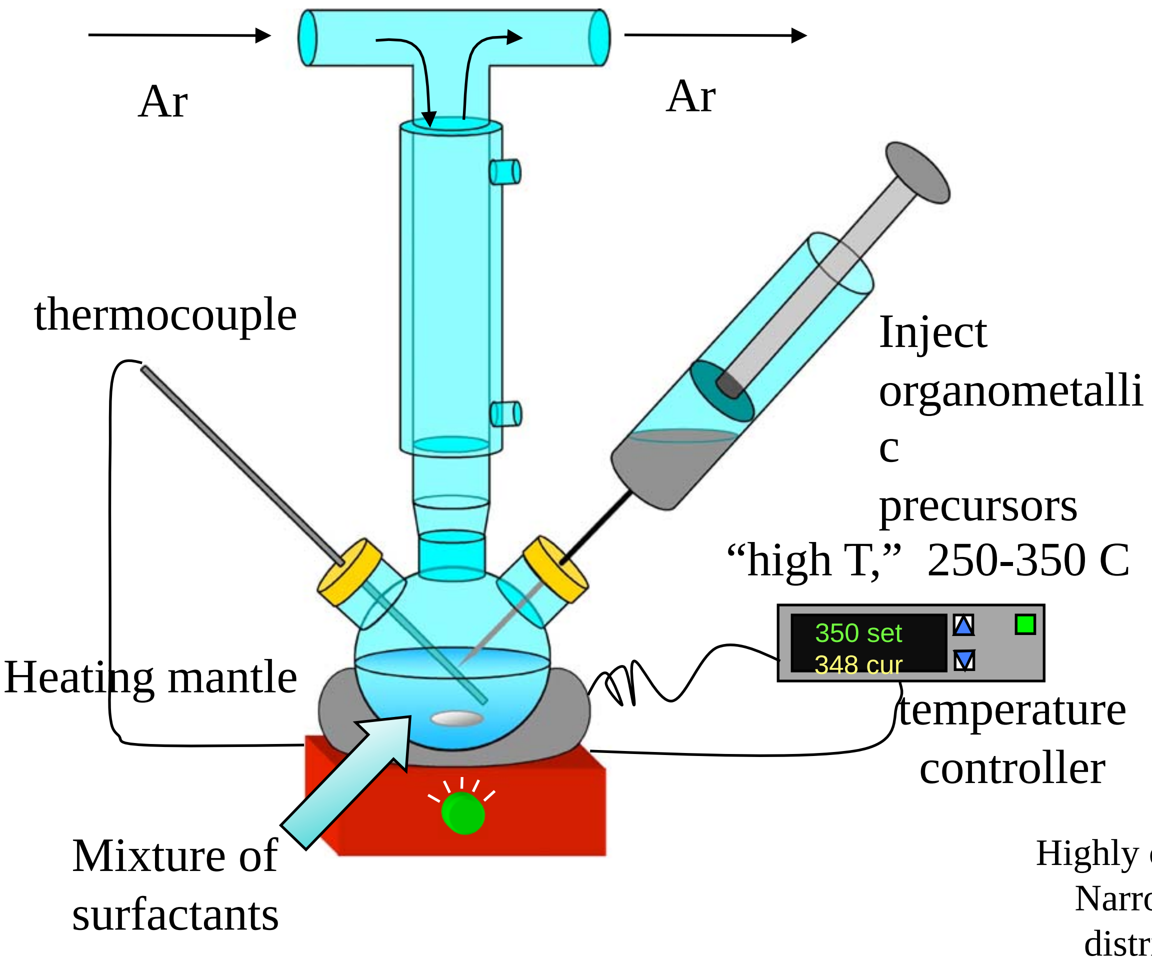
T=530 °C – Gr=0.4 ML/s

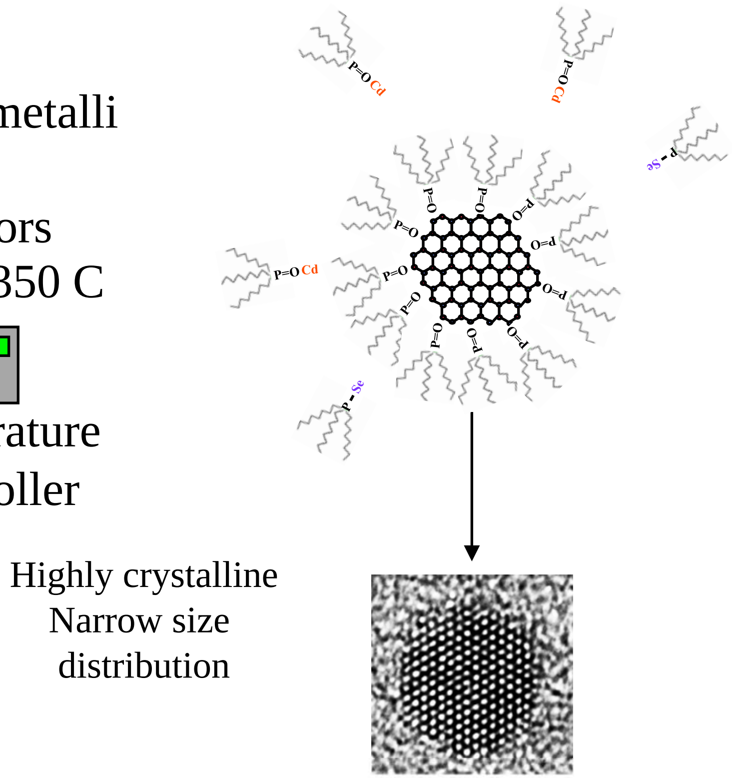


T=580 °C – Gr=0.4 ML/s

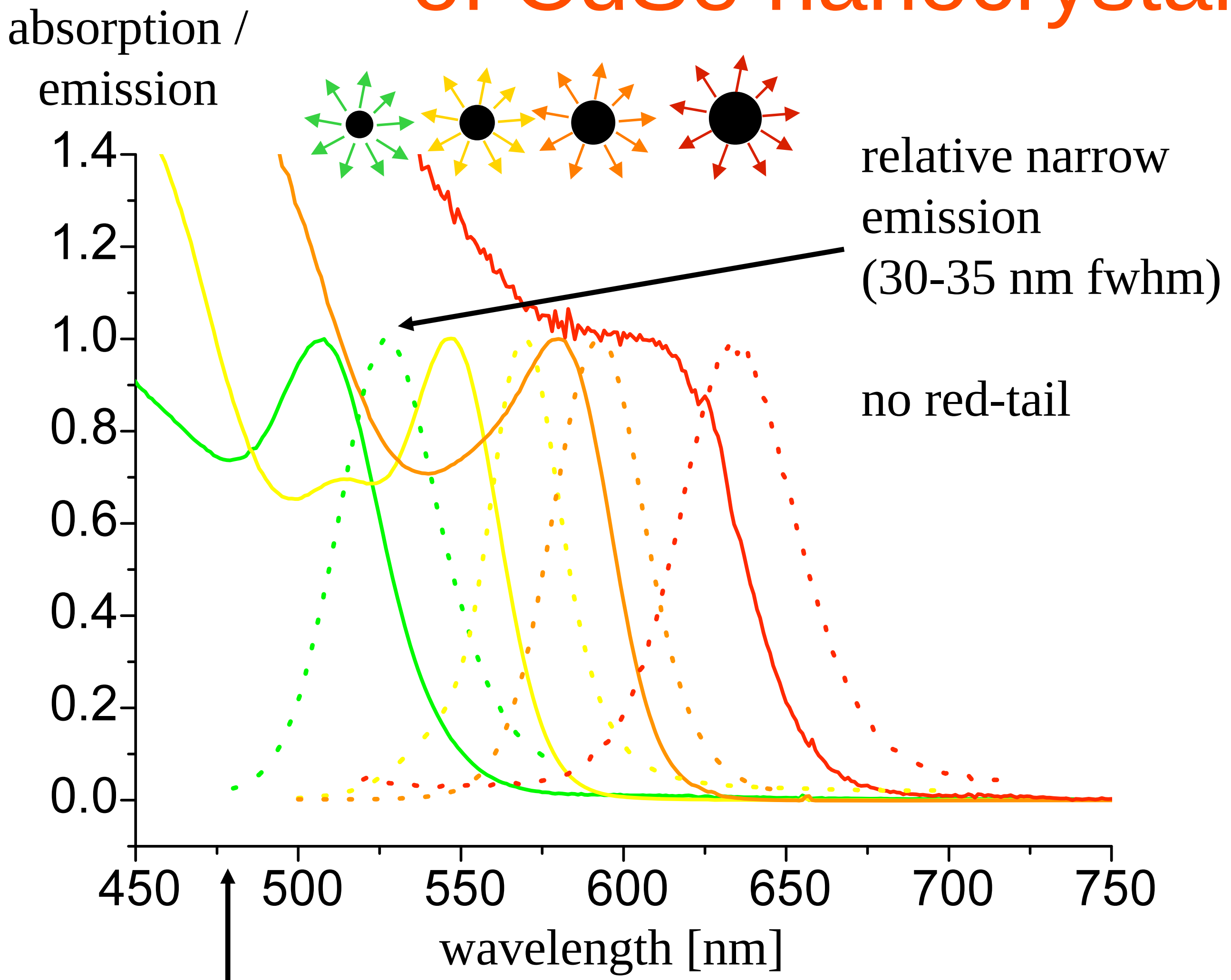
Synthesis of Colloidal Quantum dots

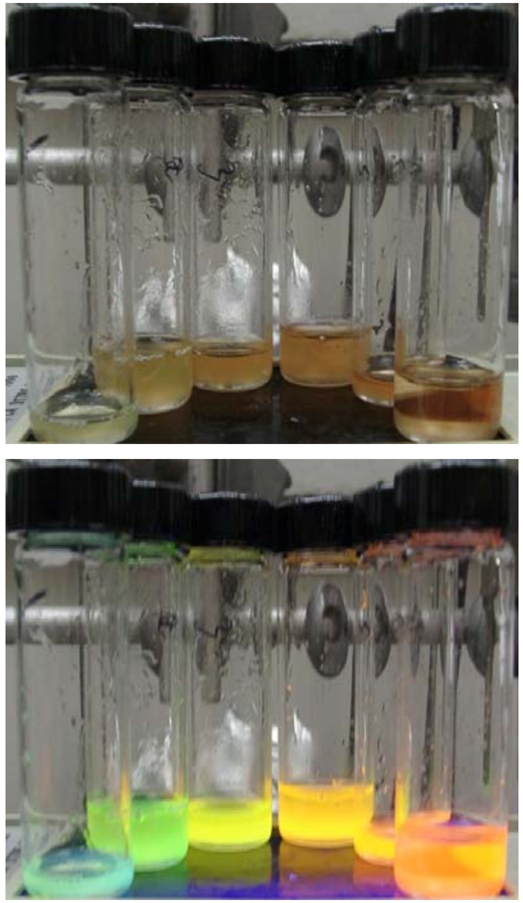
Synthesis of colloidal nanocrystals





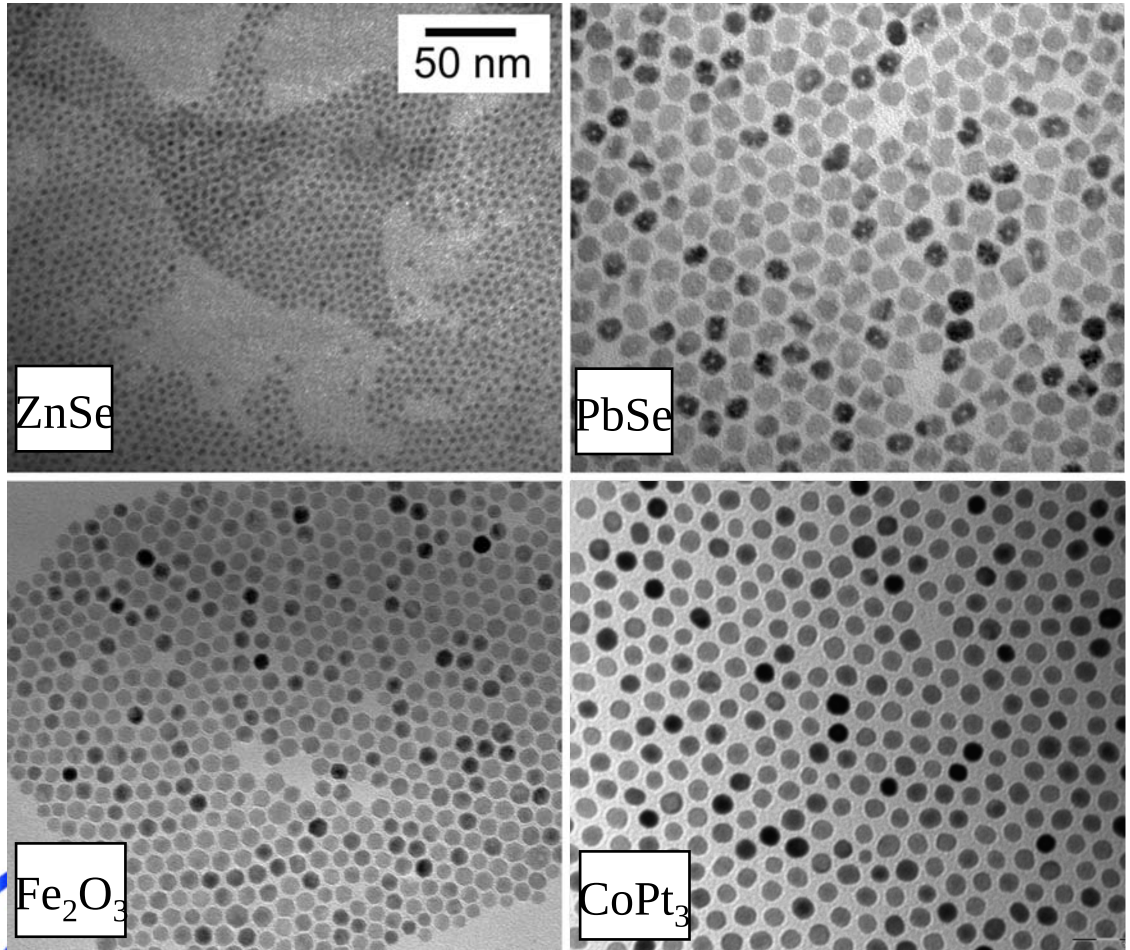
Size dependent photoluminescence of CdSe nanocrystals





all colors can be excited with one single wavelength

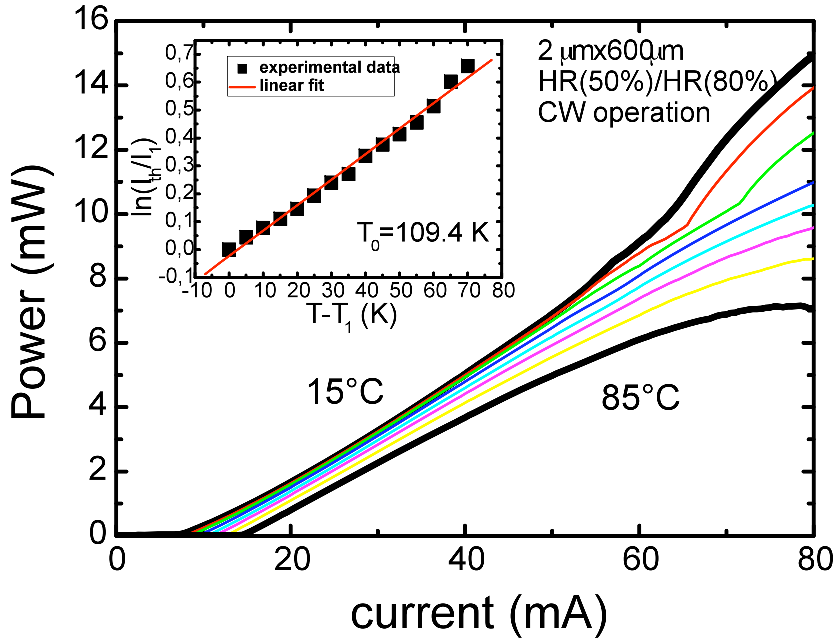
Nanocrystal size control:
Colloidal nanocrystals of different materials



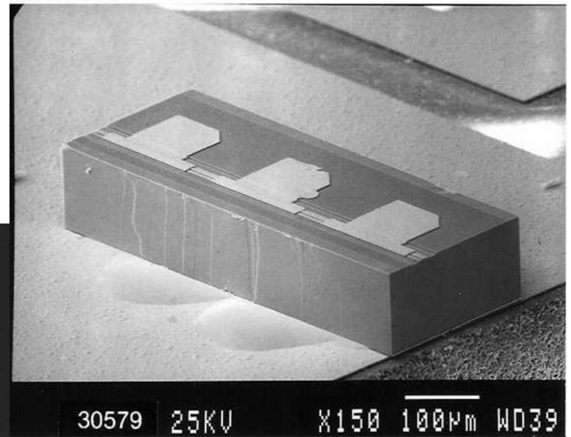
CdSe nanocrystals

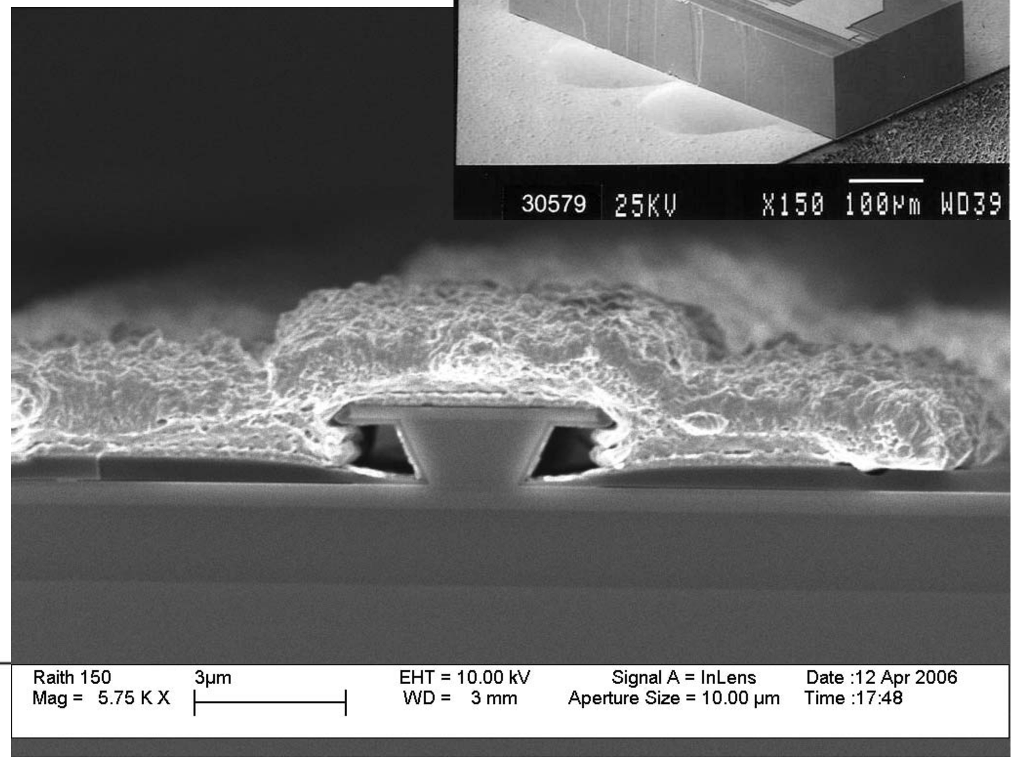
Epitaxial quantum dot devices for telecom applications

Single-mode QD lasers



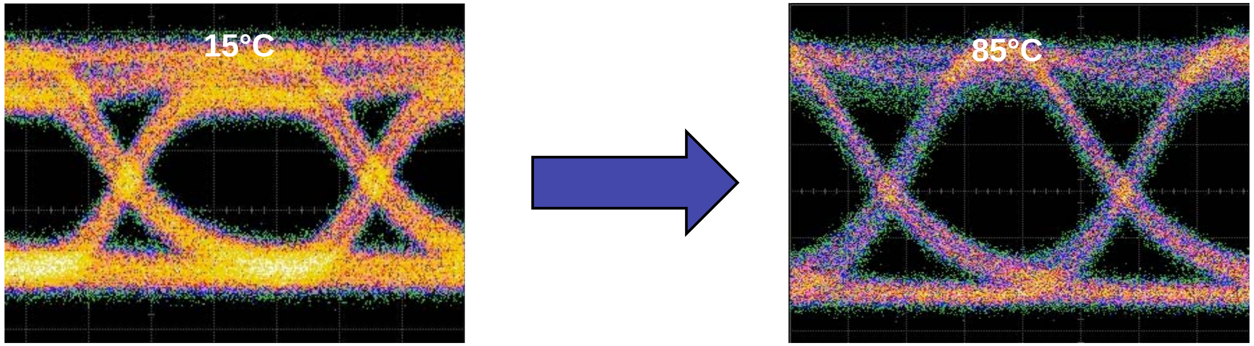
internal losses of 4.8 cm-1
internal quantum efficiency of 23%





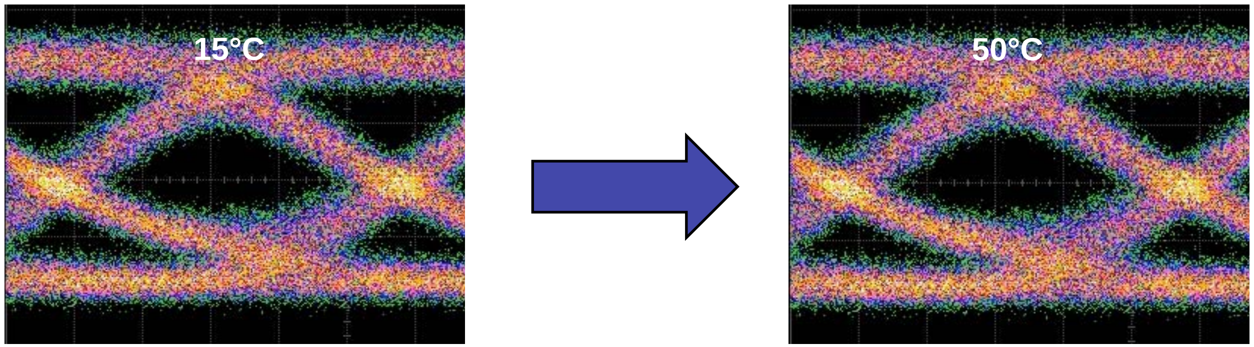
The saturation modal gain of the ground state results to be 36.3 cm^{-1} ➔ 6 cm^{-1} per QD layer

High modulation frequency eye patterns



Temperature dependence of eye patterns @ **5 Gb/s**

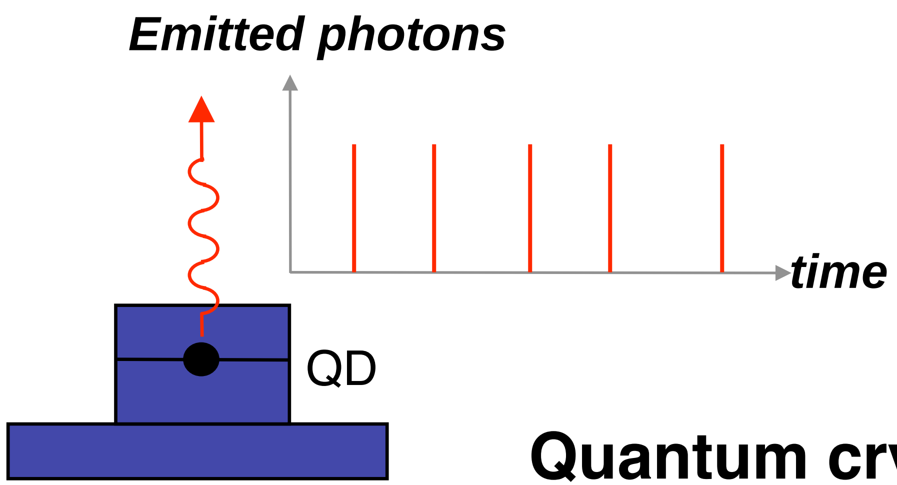
Extinction ratio of 5 dB @ 15°C and 6 dB @ 85°C



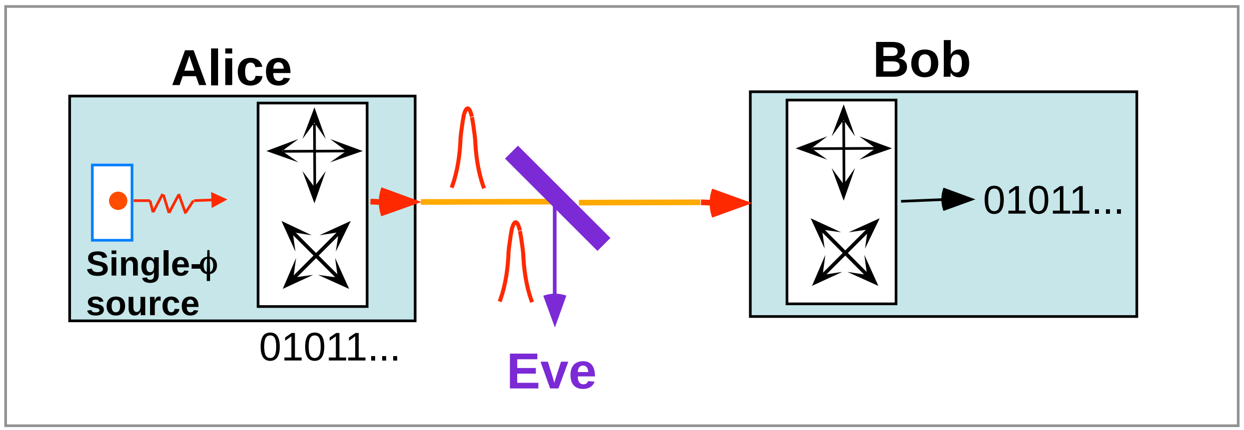
Temperature dependence of eye patterns @ **10 Gb/s**

Extinction ratio < 5 dB @ 50°C

Single photons from single QDs

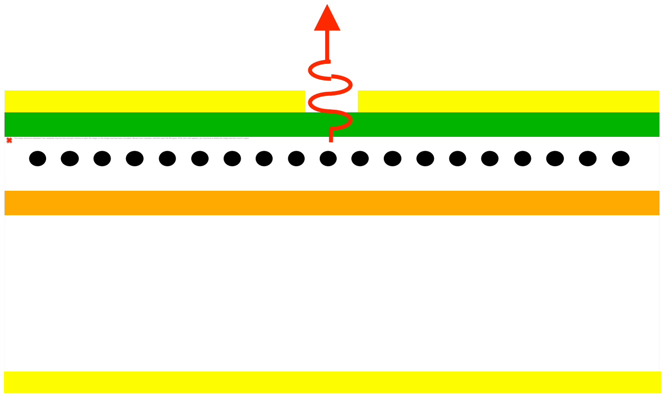


Quantum cryptography:



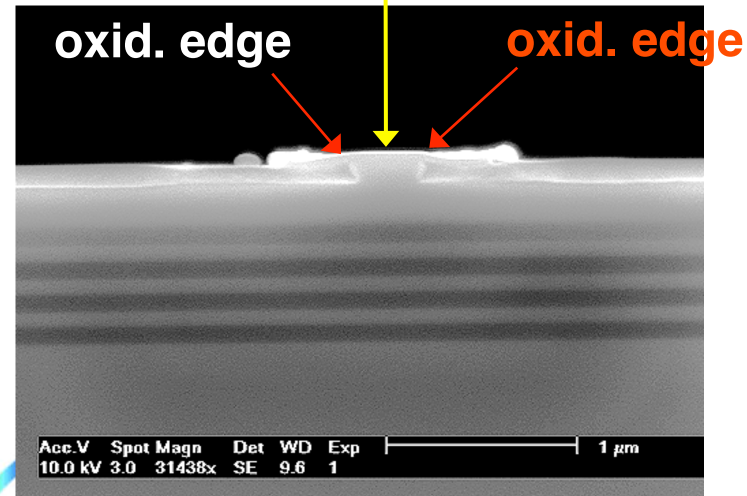
Single QD devices

Shadow-mask LED:



diffusion suppressed (<100 nm) in QDs due to carrier confinement

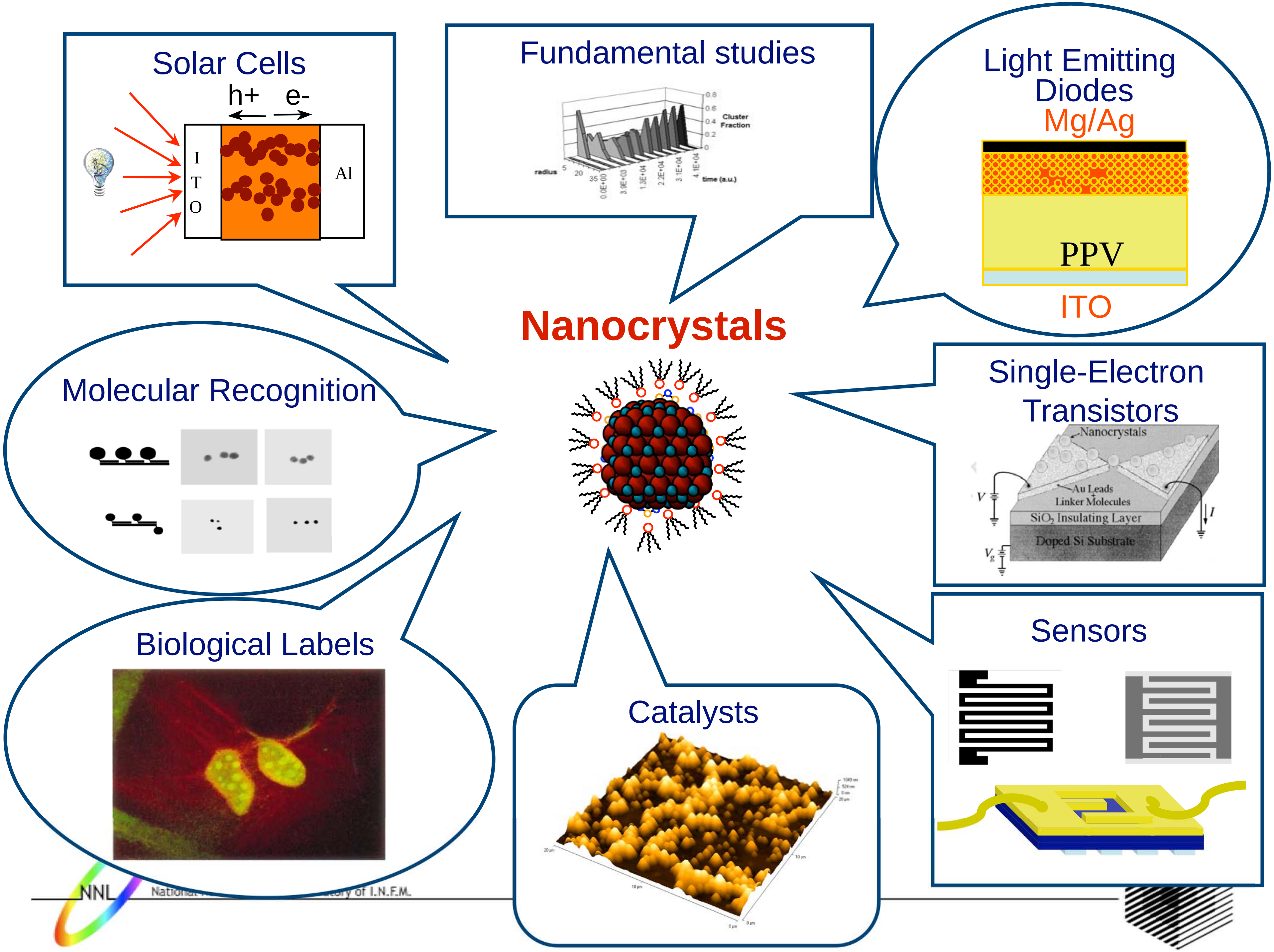
300 nm current aperture



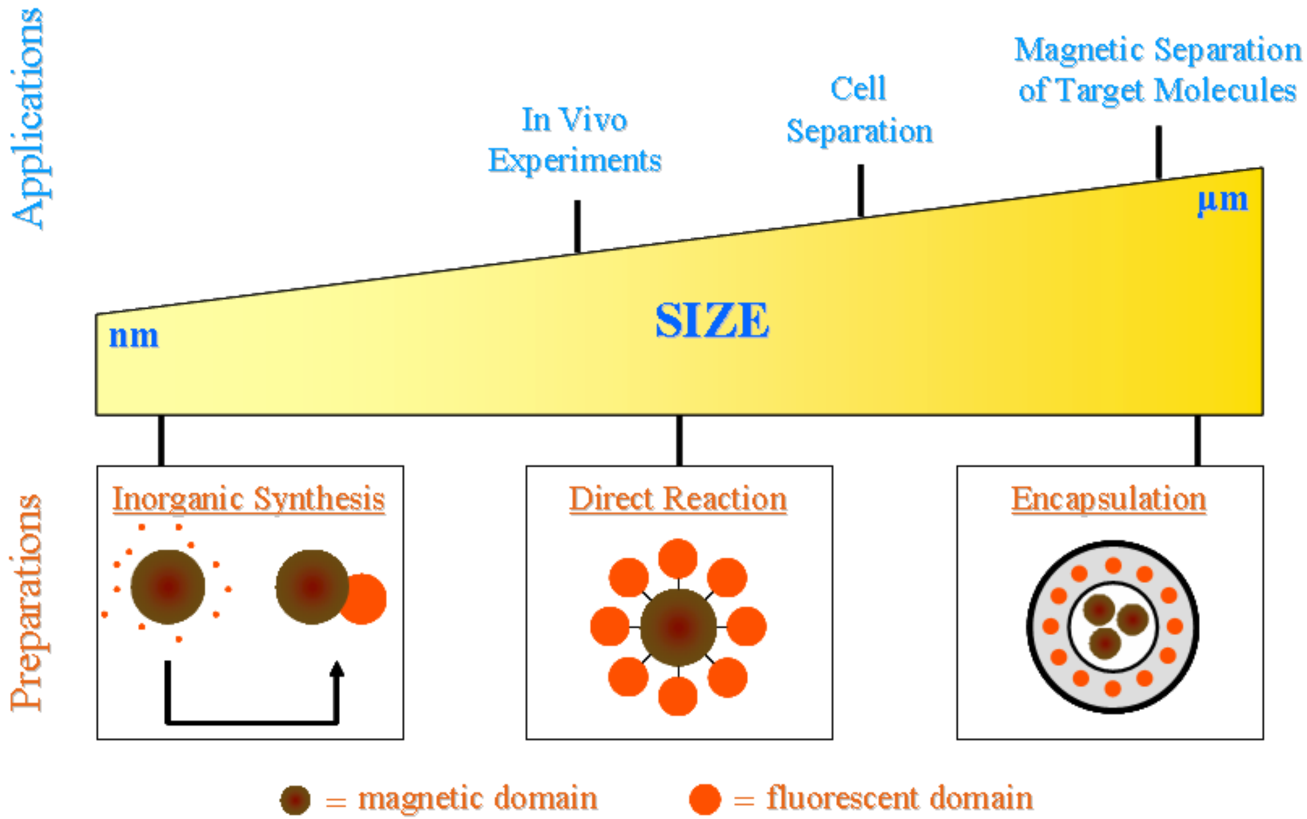
Fiore et al, Appl. Phys. Lett. 2002

- *Down to 100 nm* current apertures with simple optical lithography
- Can tailor both current and optical confinement
- Bandgap engineering to reduce current spreading

Colloidal NCs devices and applications

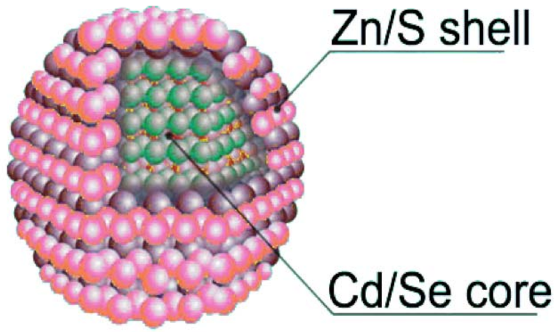

Nanocrystals
Solar Cells
h+
e-
I
T
O
Al
Fundamental studies
Cluster Fraction
radius
time (a.u.)
Light Emitting Diodes
Mg/Ag
PPV
ITO
Single-Electron Transistors
Nanocrystals
Au Leads
Linker Molecules
SiO$_2$ Insulating Layer
Doped Si Substrate
Molecular Recognition
Biological Labels
Catalysts
Sensors
NNL

Hybrid nanocomposites: magnetic and fluorescent properties combined into one single nano-object



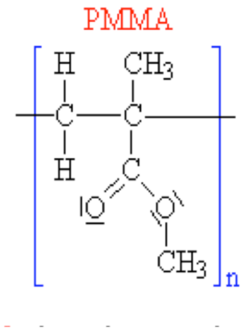
A. Quarta, R. Di Corato, L. Manna andT. Pellegrino, Fluorescent magnetic hybrid nanostructures: preparation, properties and applications in biology, IEEE Transaction in Nanobiotechnology, *in press*

NCs dispersed in resist (ER) matrix

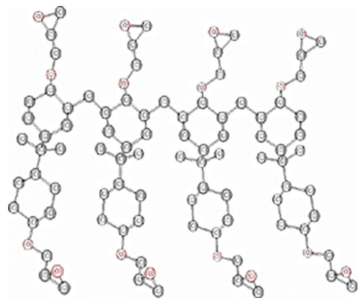


CdSe/ZnS nanocrystals

Gain material deposited by means of low-cost techniques



poly(methylmethacrylate)



SU-8(epoxy resist)

Sensitive to electron beam or UV radiation

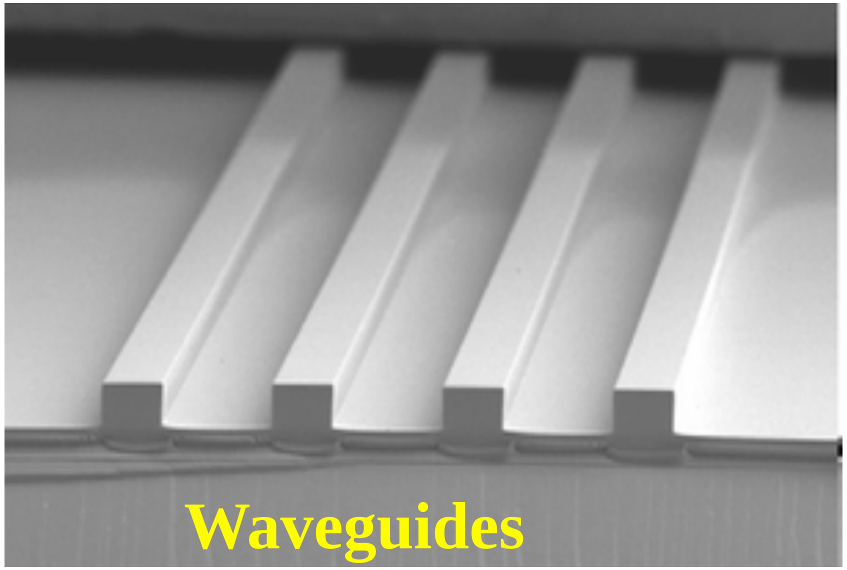
Highly versatile active material for optical devices

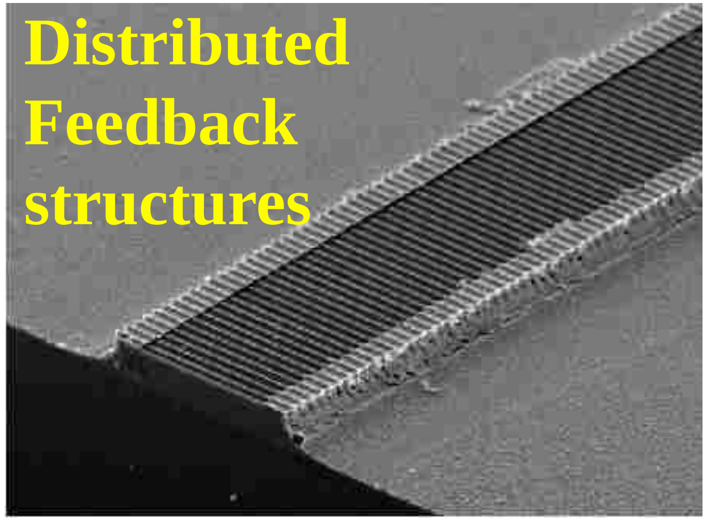
- Decoupled synthesis of NCs from preparation of matrix

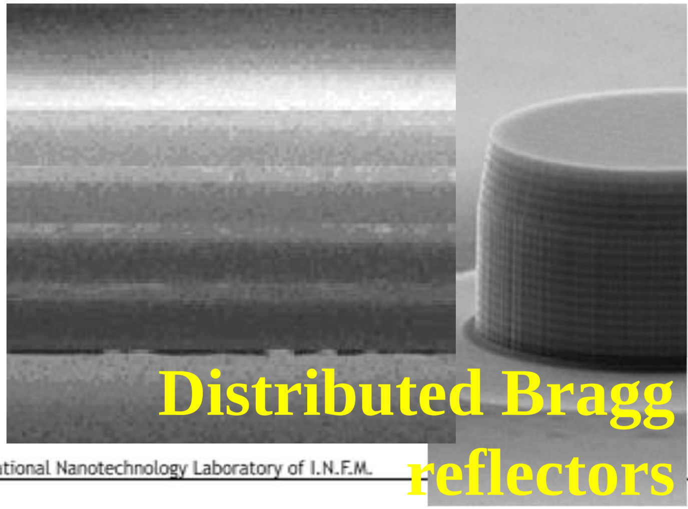
-Complete tunability of optical properties from UV to IR range

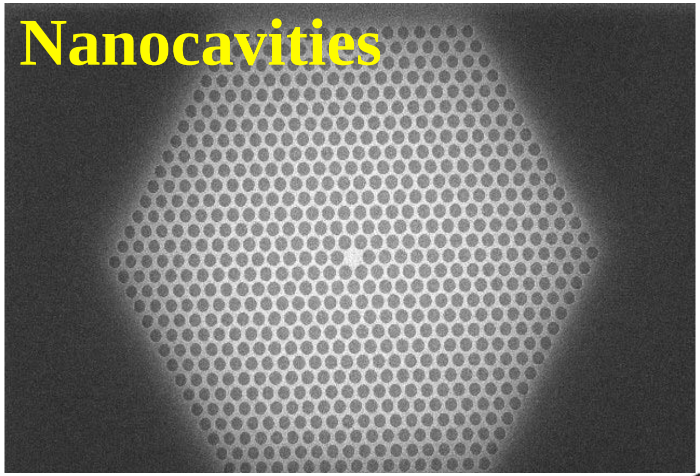
- Full control on the device geometry/Selective localization of emitters with nanometer scale resolution

Building blocks for photonic devices

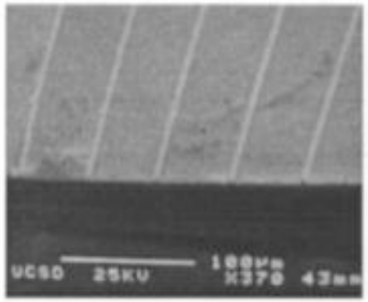




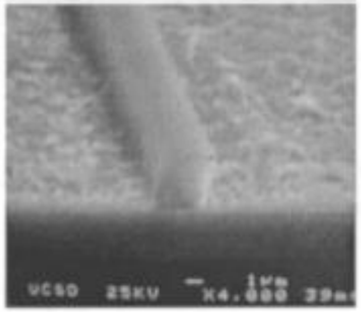




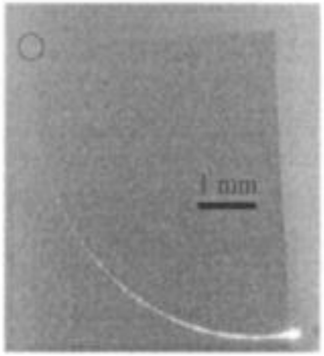
Building blocks for photonic devices



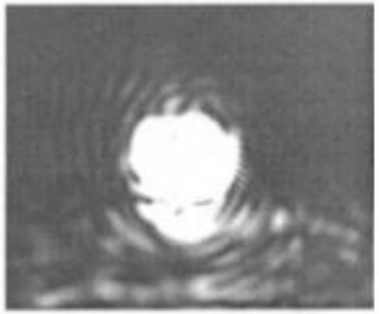
(a)



(b)



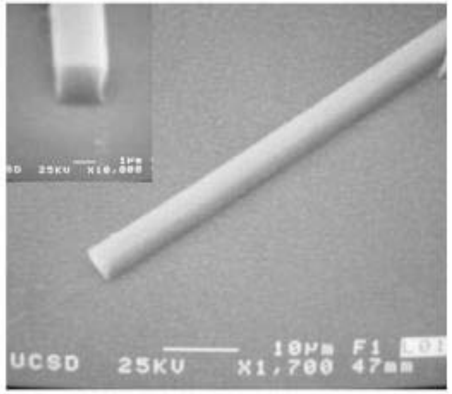
(c)



(d)

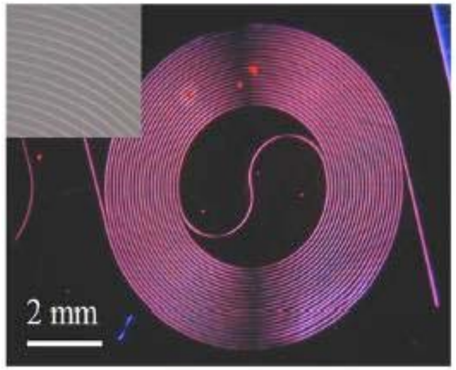
PMMA/NCs

Waveguides



(a)

SU-8/NCs

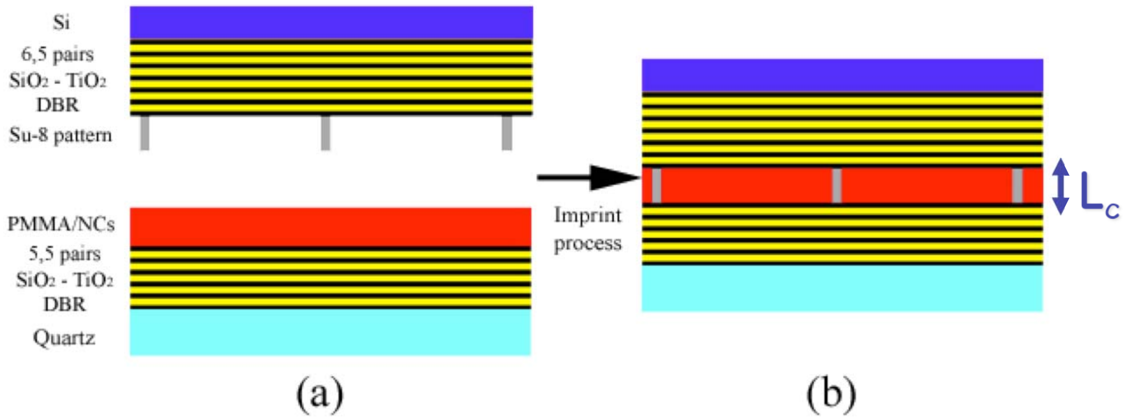


(b)

L.Pang et al., *"Photosensitive quantum dot composites and their applications in optical structures"*, J. Vac. Sci. Technol. B 23, p. 2413 (2005)

Colloidal QDs: vertical microcavity by hot embossing

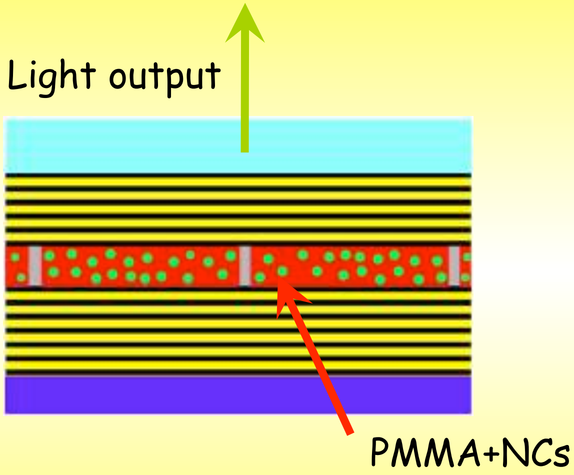
- Unconventional use of **hot embossing** techniques
- **Colloidal CdSe/ZnS nanocrystals dispersed in a polymeric matrix (PMMA)**
- **Thermoplastic behavior of PMMA** exploited in order to define the device geometry

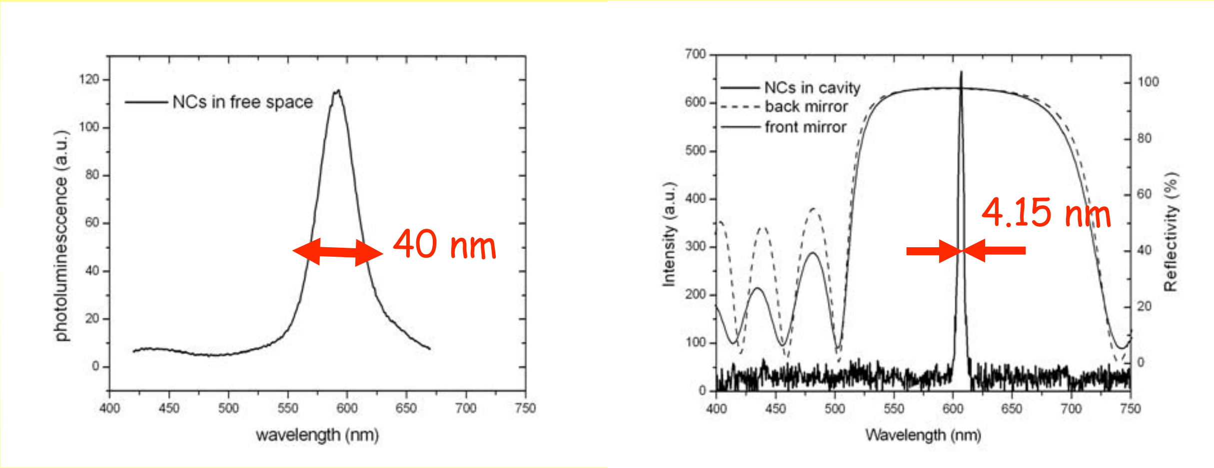


High-temperature exposure: 10' to 180°C ➔ **No damage of the optical properties of QDs**

Insertion of SU-8 spacers between the mirrors ➔**Good control of the cavity length L_c**

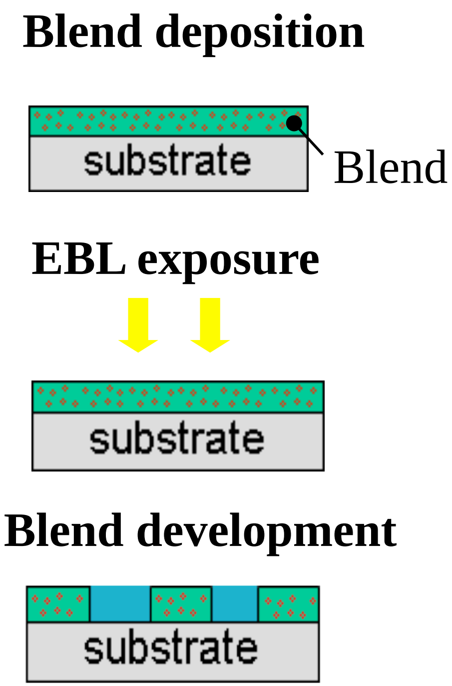
Colloidal QDs: hybrid vertical microcavity by hot embossing

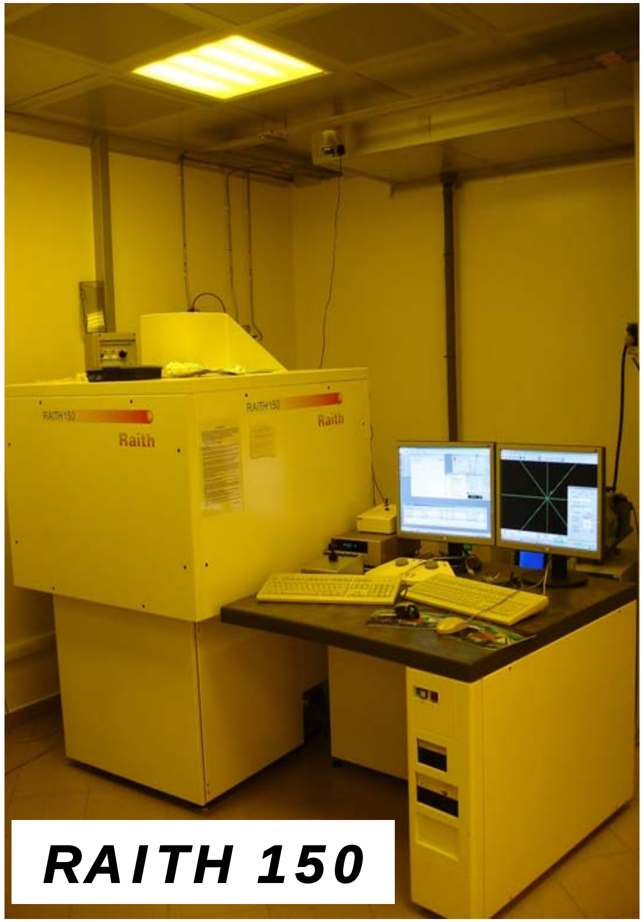




Q = 146

Localization of NCs by EBL processes



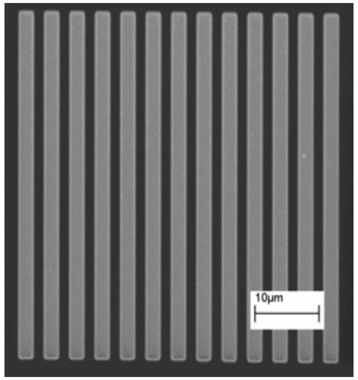


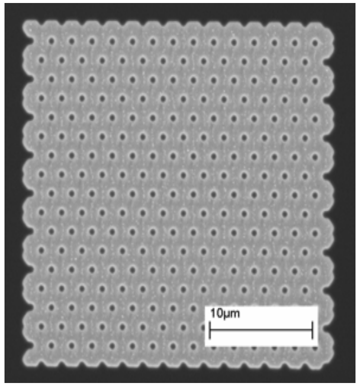
- Polymer/NCs blend still behaves as a resist
- Emission properties of NCs must not be affected by electron beam exposures

L. Martiradonna et al., *Microelectron. Eng.*, 83, 1478-1481, 2006.

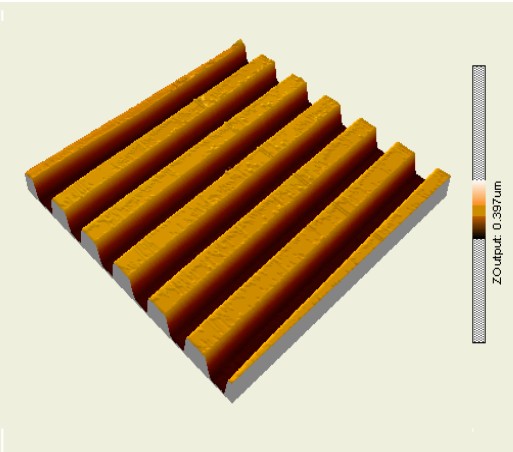
SEM and AFM images of patterned blend

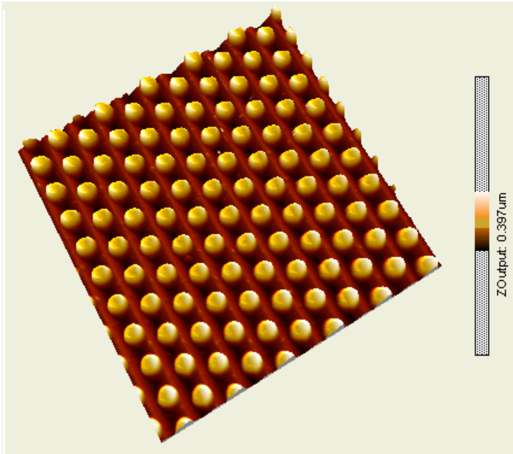
Stripes:
width=2μm
period=4μm





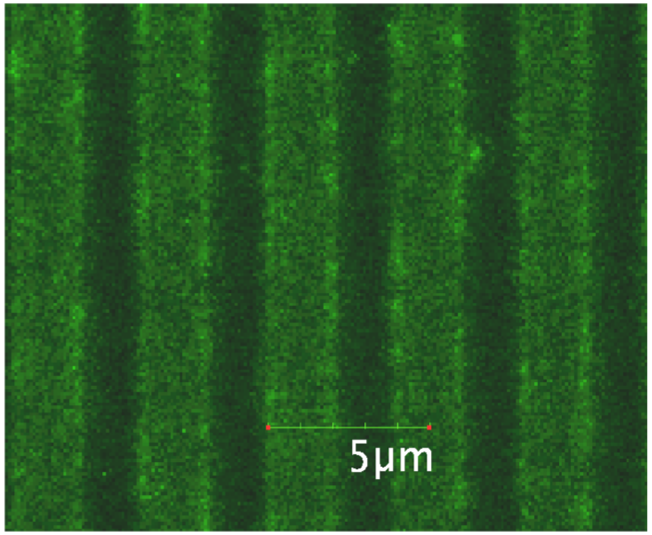
Pillars:
diameter=0.6μm
Period=2μm

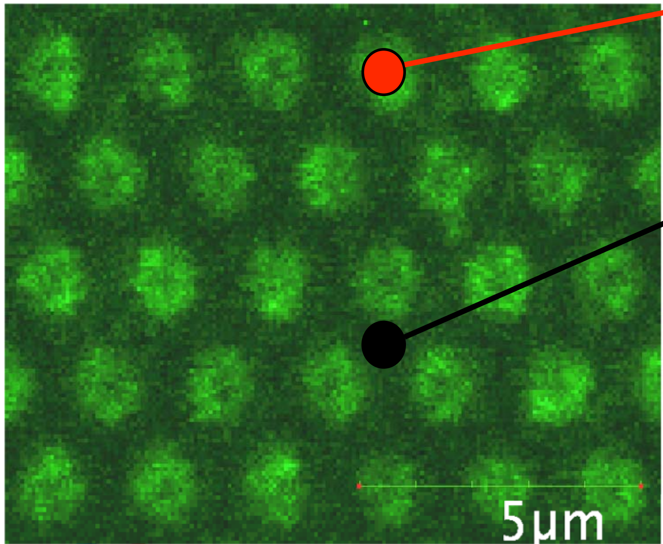


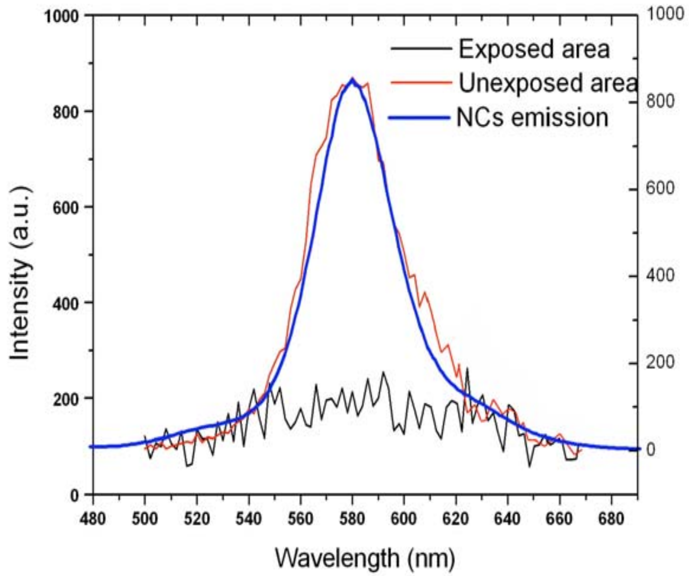


<u>The positive resist behaviour of PMMA is not perturbed by the presence of NCs</u>

Photoluminescence maps by confocal microscope







The emission spectrum of NCs is not affected by EBL

PL signal is detected only in the unexposed regions

NCs localization by lithographic techniques

Several advantages:

- any kind of substrate without recurring to chemical or physical treatment of the surfaces;

- not only rigid substrates but also flexible devices;

- the typical resolution is defined by the lithographic process;

- the density of emitters can be easily tuned by varying the relative molar concentration of the two components (NCs – resist);

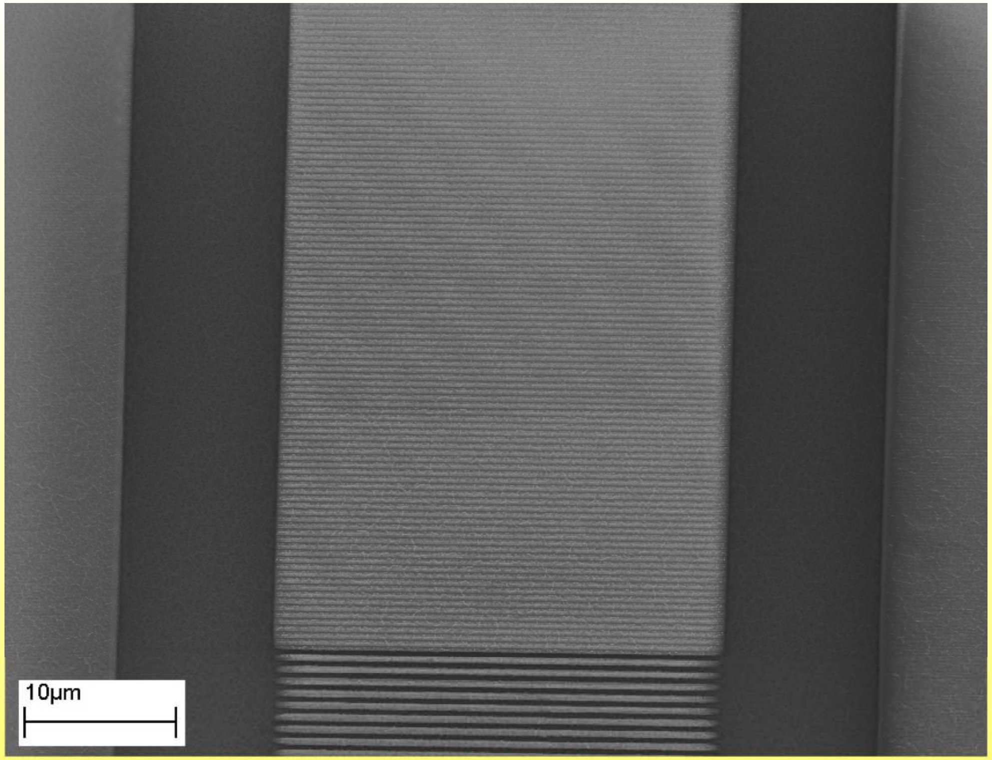
- processing by standard photolithographic techniques;

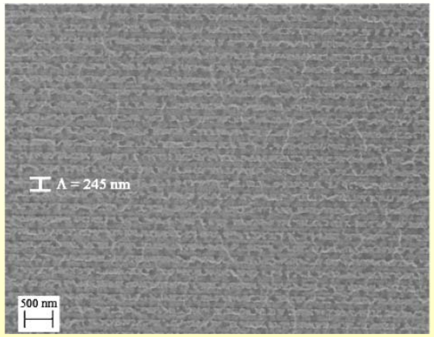
- refractive index of the blend tunable with the NCs concentration.

Colloidal QDs:

Patterning of colloidal QDs by lithographic techniques

Building blocks for photonic devices

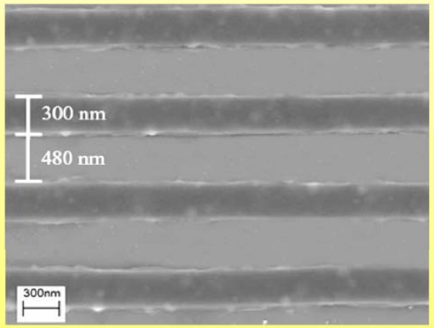




DFB

L_{BRAGG} = 245 nm

thk = 40 nm



DBR

3λ/4

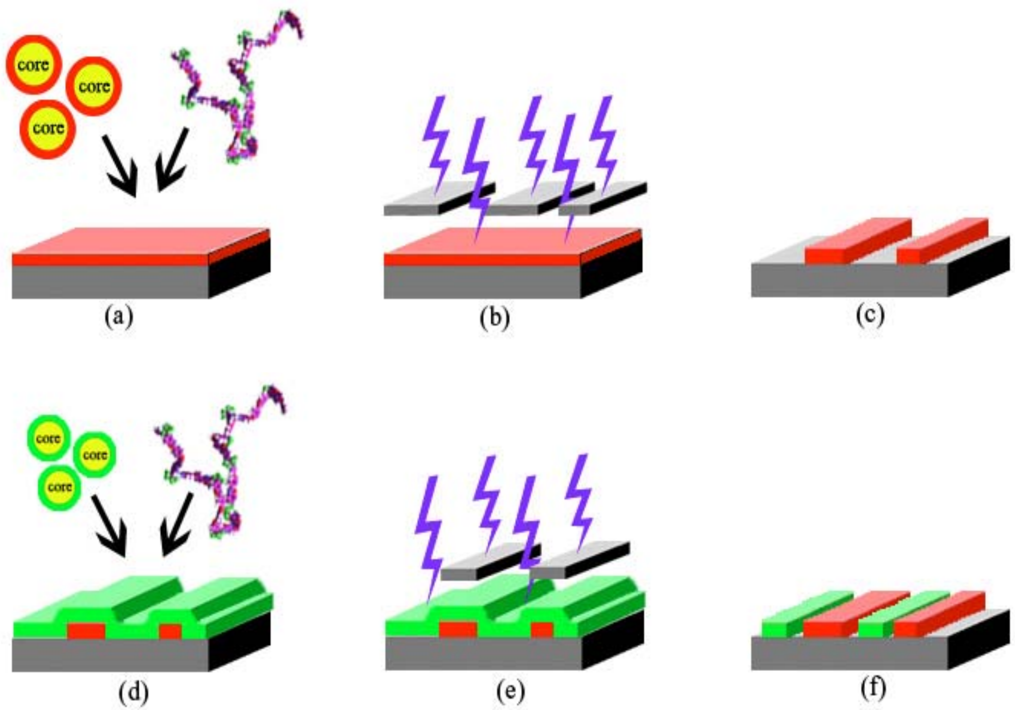
stripes

thk = 400nm

Easy implementation of multi-wavelength devices

lithographic process on 1st NCs ensemble

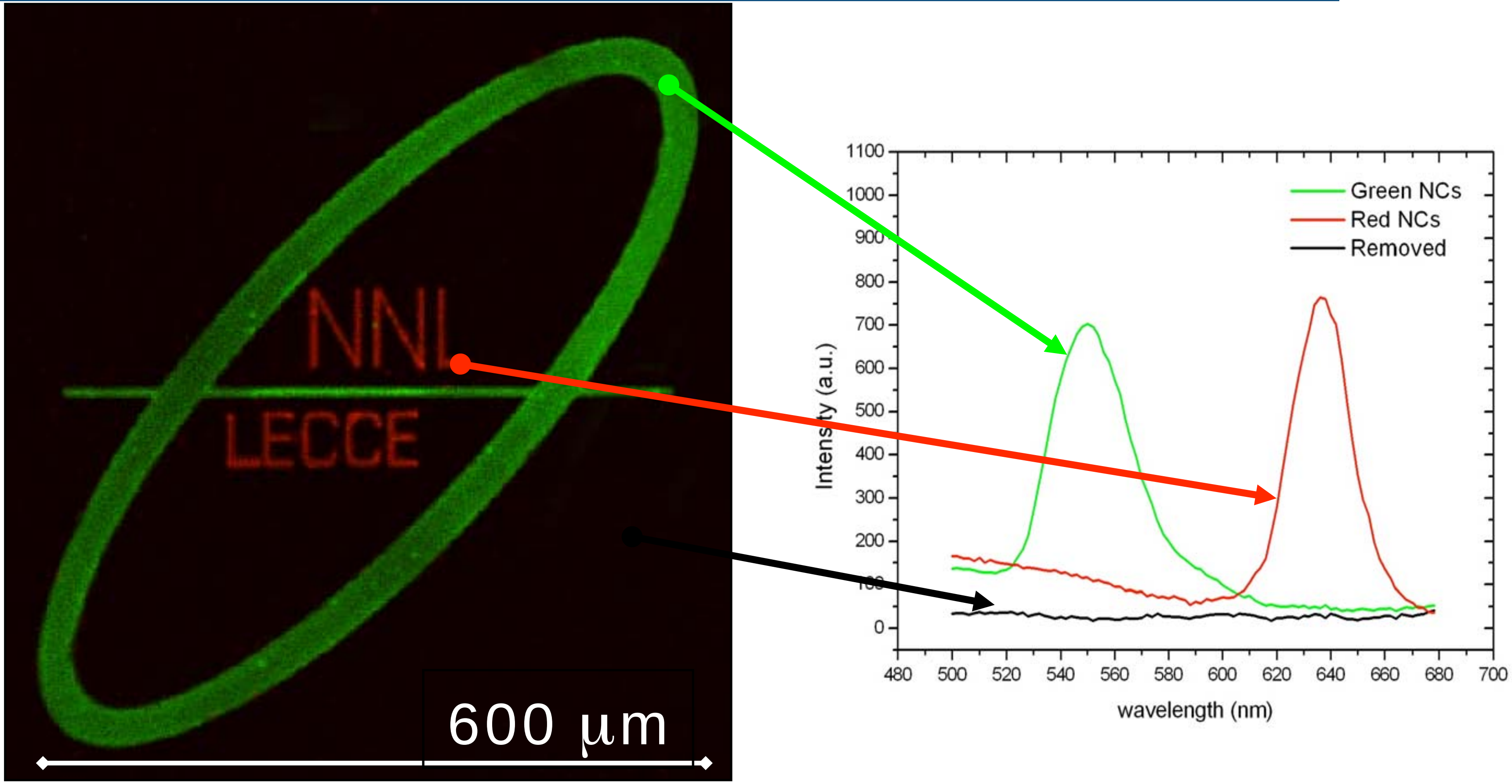
aligned lithographic process on 2nd NCs ensemble



Re-aligned lithography

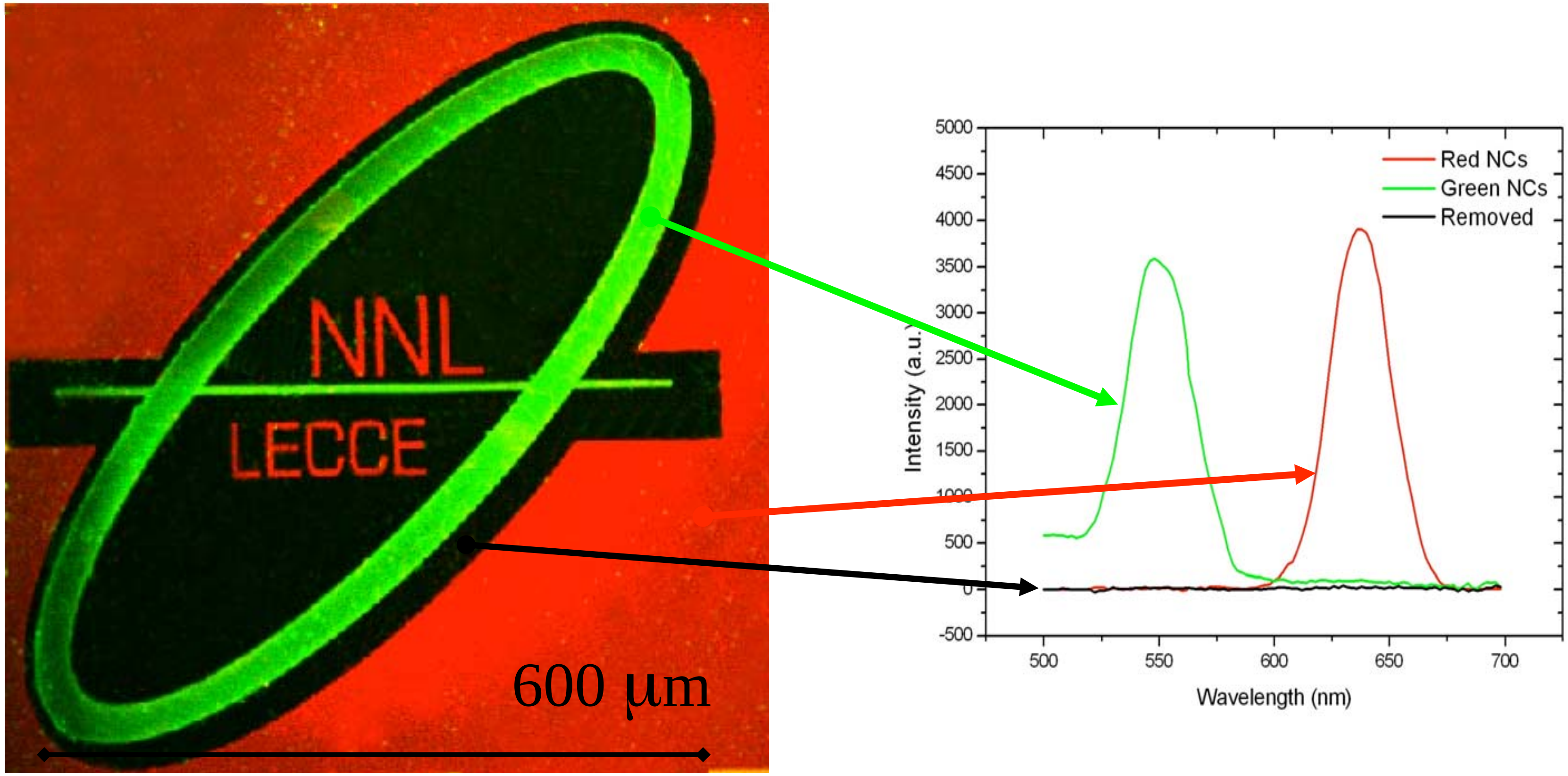
Localization of NCs emitting at different wavelengths on near or superimposed regions

Easy implementation of multi-wavelength



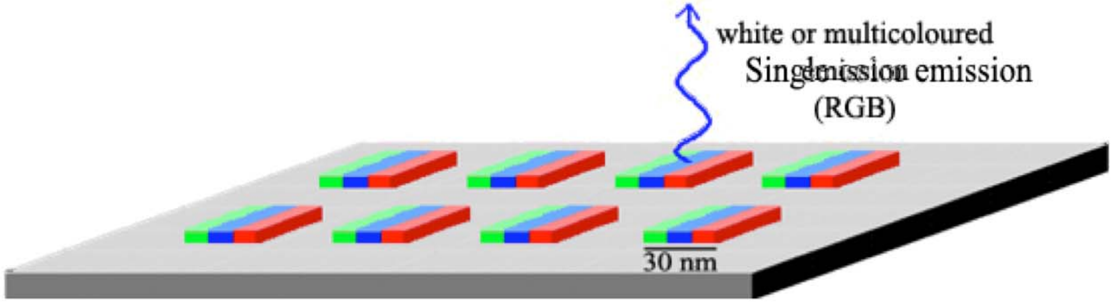
- **1st lithography: SU-8/red NCs** (λ_{peak}=640 nm, $M_{NCs}=3.5\cdot10^{-6}$ mol/l)
- **2nd lithography: SU-8/green NCs** (λ_{peak}=550 nm, $M_{NCs}=7.2\cdot10^{-6}$ mol/l)

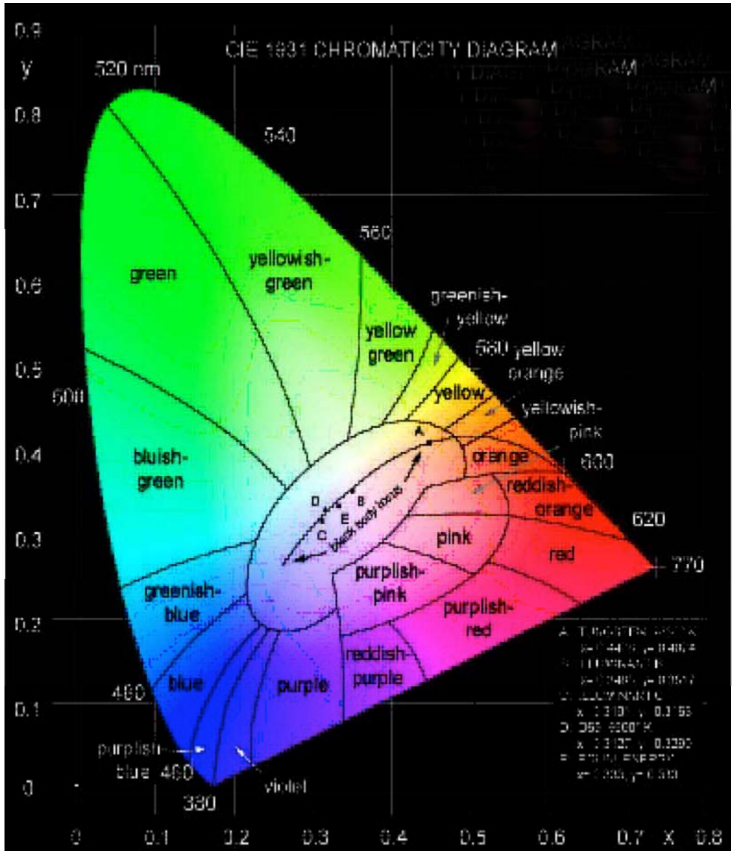
Easy implementation of multi-wavelength



- **1st e-beam lithography: PMMA/red NCs** (λ_{peak}=640 nm, $M_{NCs}=2.5\cdot10^{-5}$ mol/l)
- **2nd photolithography: SU-8/green NCs** (λ_{peak}=550 nm, $M_{NCs}=7.2\cdot10^{-6}$ mol/l)

Easy implementation of multi-wavelength devices





Single colour nanopixels

Multicoloured nanopixels

White emitting nanopixels

Relative intensities of R, G and B tunable with NCs concentration and pattern dimensions