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COLLOIDAL NANOCRYSTAL BASED PHOTONIC DEVICES FABRICATION

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Roberto Cingolani and Massimo De Vittorio

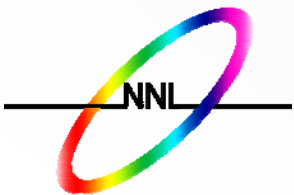
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Outline

- **Colloidal nanocrystals (NCs): active materials for high-performing photonic devices**
- **Processing of NCs: from close-packed to NCs in blends**
- **NCs in resist blends**
- **Building blocks for photonic devices based on colloidal NCs**
- **Conclusions**



Colloidal nanocrystals

- Chemically synthesized Quantum Dots
- Low fabrication costs with high throughput



MOCVD

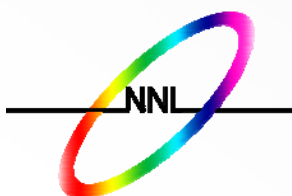
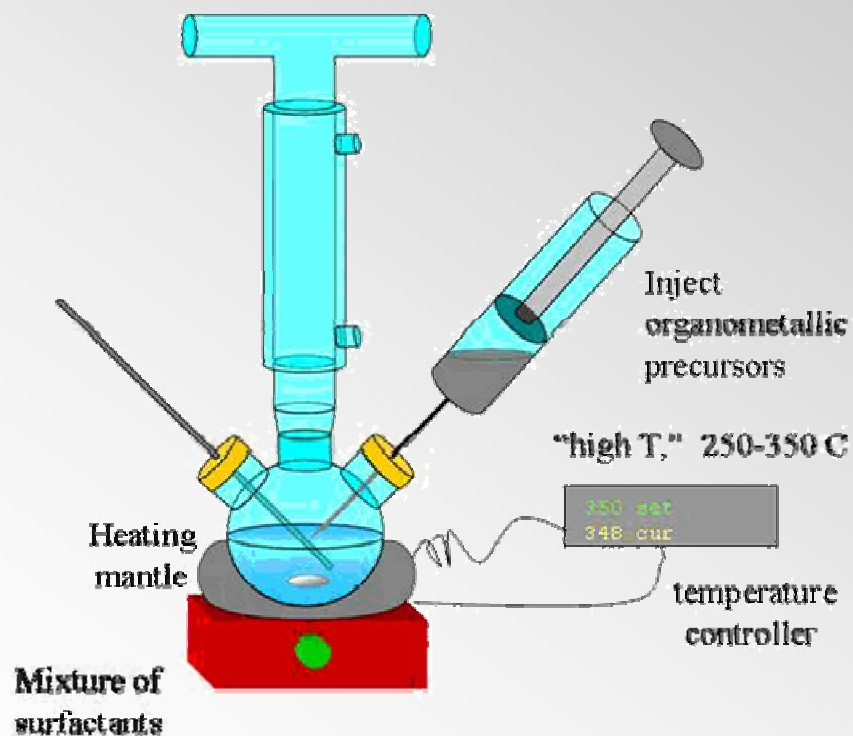


MBE



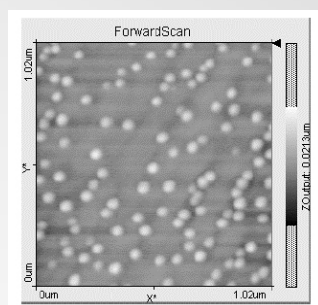
Colloidal nanocrystals

- Chemically synthesized Quantum Dots
- Low fabrication costs with high throughput

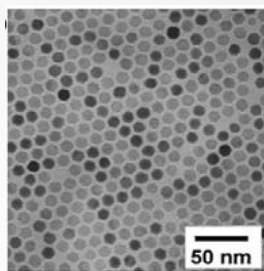


Colloidal nanocrystals

- Chemically synthesized Quantum Dots
- Low fabrication costs with high throughput
- Low dimensions – strongly size-dependent optical behavior
- Thermal stability

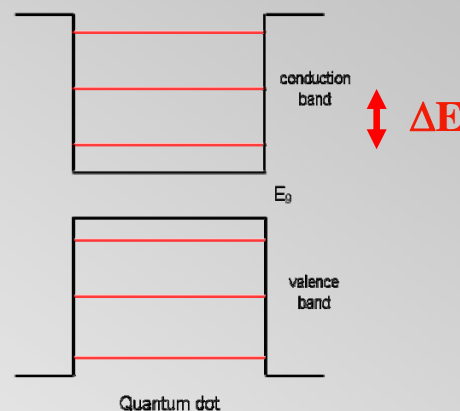


$d \sim 40\text{-}50 \text{ nm}$

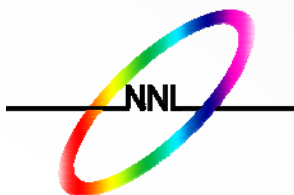
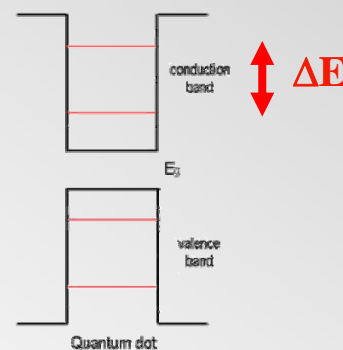


$d \sim 2\text{-}6 \text{ nm}$

Epitaxial QDs

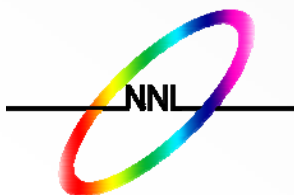
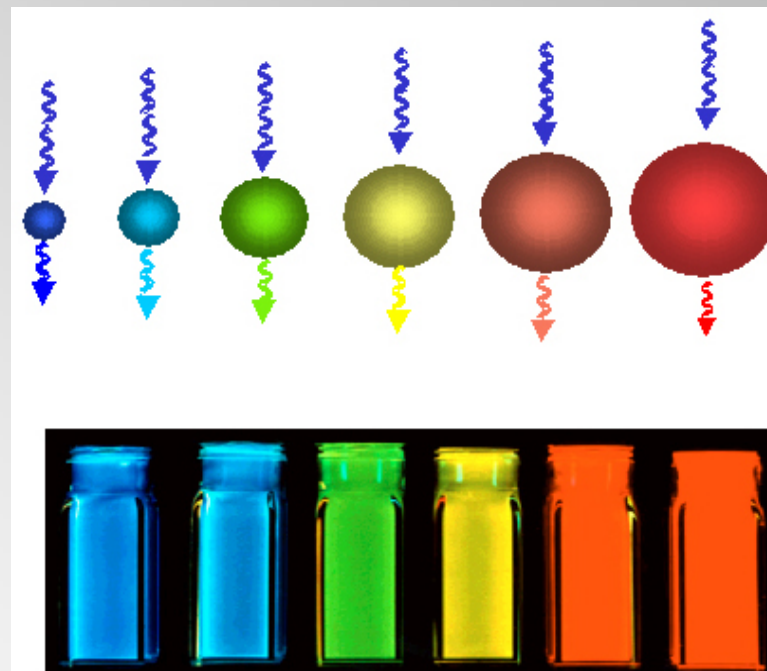


Colloidal QDs



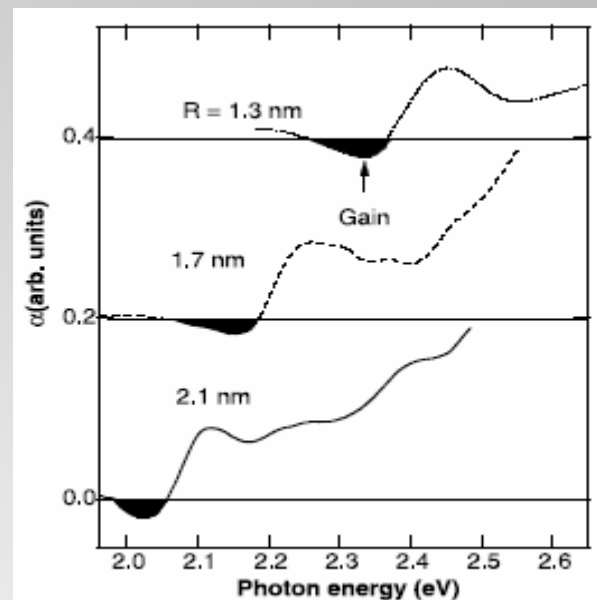
Colloidal nanocrystals

- Chemically synthesized Quantum Dots
- Low fabrication costs with high throughput
- Low dimensions – strongly size-dependent optical behavior
- Thermal stability
- Full tunability from UV to IR



Colloidal nanocrystals

- Chemically synthesized Quantum Dots
- Low fabrication costs with high throughput
- Low dimensions – strongly size-dependent optical behavior
- Thermal stability
- Full tunability from UV to IR
- Optical gain and stimulated emission
 - ↳ High volume fractions
 - ↳ Close-packed films



V.I.Klimov et al., "Optical gain and stimulated emission in nanocrystal quantum dots", *Science* **290**, p.314 (2000)



Close-packed films / NCs in Titania blends

- Rough films – chaotic networks of cracks
 - ↳ low optical quality – high scattering losses
 - ↳ how to process them?



NCs dispersed in titania matrix

- V.C. Sundar et al. “*Room-temperature, Tunable Gain Media from Novel II-VI Nanocrystal-Titania Composite Matrices*”, *Adv. Mater.*, **14**, p.739 (2002)
- M. A. Petruska et al. “*High-Performance, Quantum Dot Nanocomposites for Nonlinear Optical and Optical Gain Applications*”, *Adv. Mater.* **15**, p. 610 (2003)



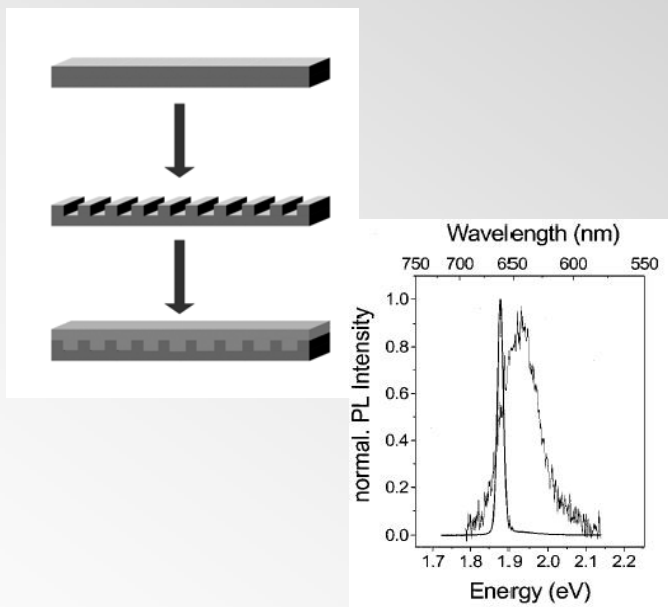
NCs in Titania blends

- Decoupled synthesis of NCs from preparation of matrix
- Sol-gel technique under inert atmosphere
- Surface-chemistry improved to obtain high volume fractions ($> 1\%$ as required for Amplified Spontaneous Emission) with no phase separation
- Concentration of NCs exploited to tune the refractive index from 1.6 to 1.8
- low-scattering waveguiding films
- ASE signal demonstrated at low Temperature and Room Temperature



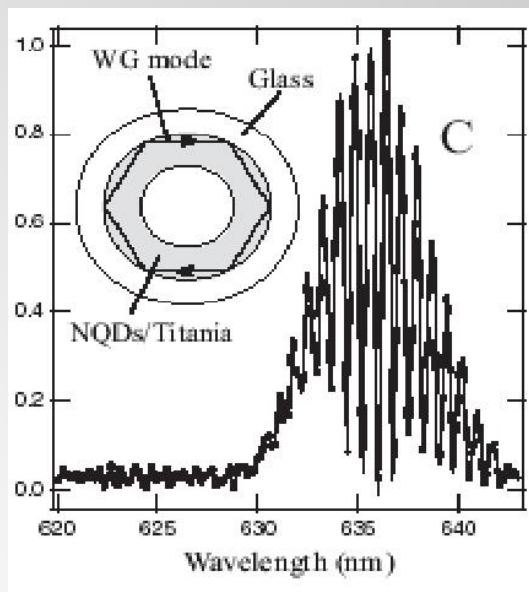
NCs in Titania Blends

Etching of the substrate



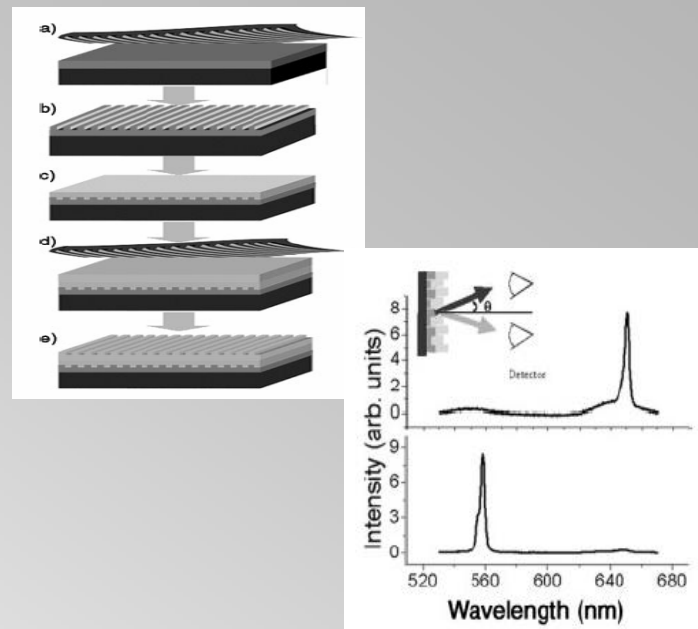
H. J. Eisler, V. C. Sundar, M. G. Bawendi,
M. Walsh, H. I. Smith, and V. Klimov,
Appl. Phys. Lett., 80, p. 4614 (2002)

Glass capillaries

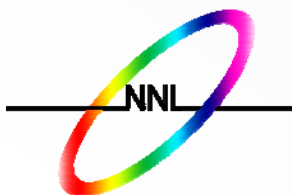


M.A. Petruska, A.V. Malko, P.M. Voyles and V. Klimov,
Adv. Mater., 15, p.610 (2003)

Soft-lithography



V. C. Sundar, H. J. Eisler, T. Deng, Y. Chan,
E. L. Thomas, and M. G. Bawendi,
Adv. Mater., 16, p. 2137 (2004)



NCs in Titania Blends

Limited freedom in the definition of the photonic device geometry

-Ridge-like geometries ?

└ imprint limited by bottom residual layers

└ pre-patterning of substrates

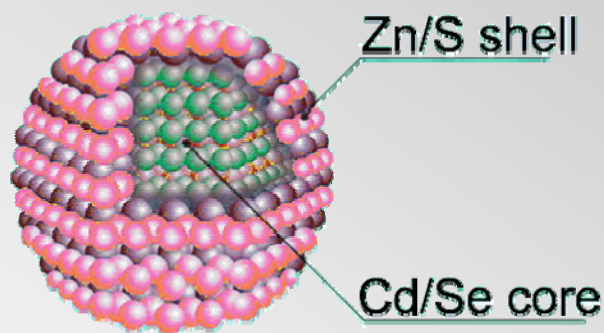
- Need of rigid substrates

- Maximum index contrast: ~ 0.3 on glass

- Multi-wavelength devices on the same substrate: only stacked configurations

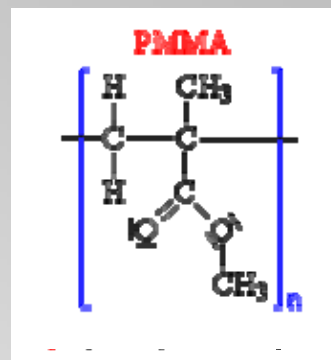


NCs dispersed in resist matrix



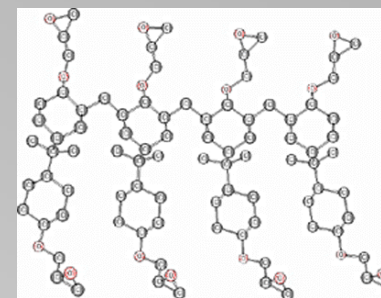
CdSe/ZnS
nanocrystals

Gain material synthesized by
means of low-cost techniques



poly(methylmethacrylate)

Sensitive to electron beam or UV radiation

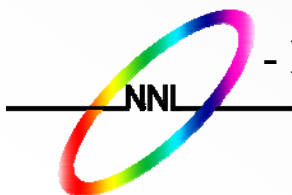


SU-8 (epoxy resist)



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

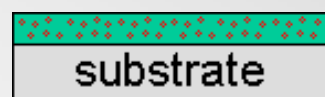


Localization of NCs by EBL processes

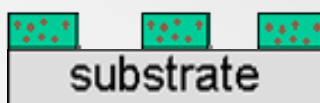
Blend deposition



EBL exposure



Blend development

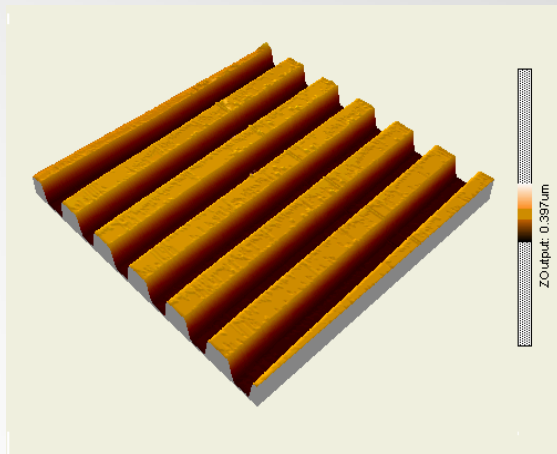
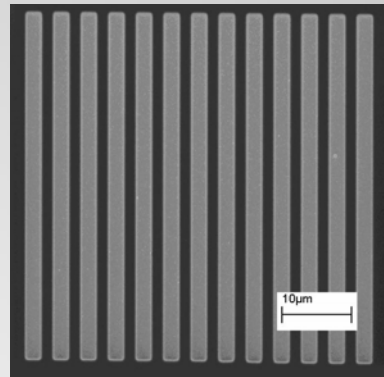


- Polymer/NCs blend still behaves as a resist
- Emission properties of NCs must not be affected by electron beam exposures

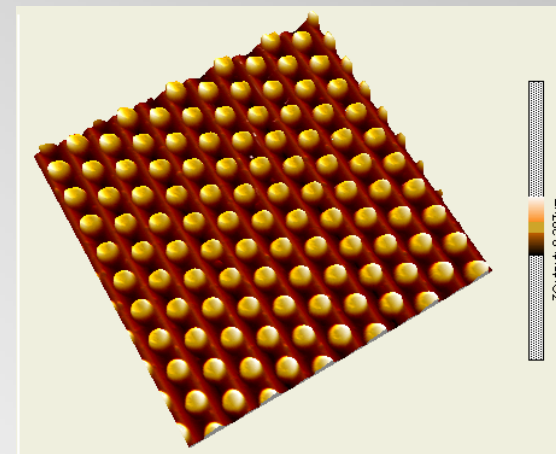
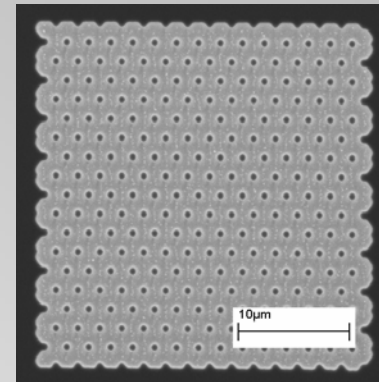


SEM and AFM images of patterned blend

Stripes:
width= $2\mu\text{m}$
period= $4\mu\text{m}$



Pillars:
diameter= $0.6\mu\text{m}$
Period= $2\mu\text{m}$

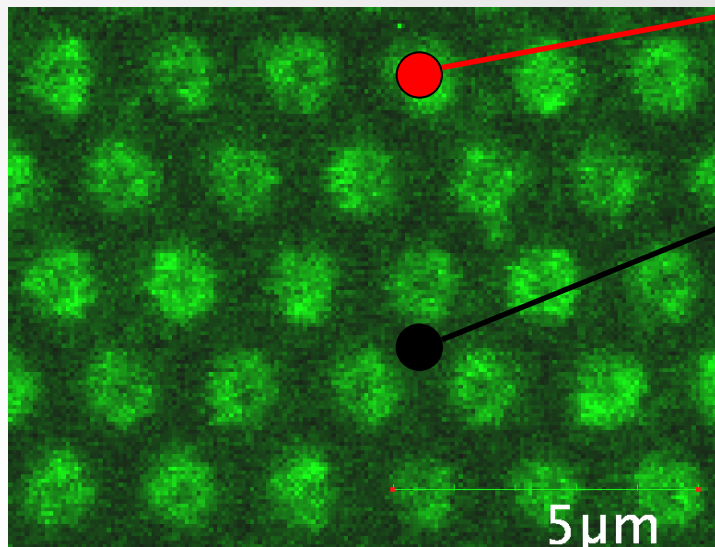
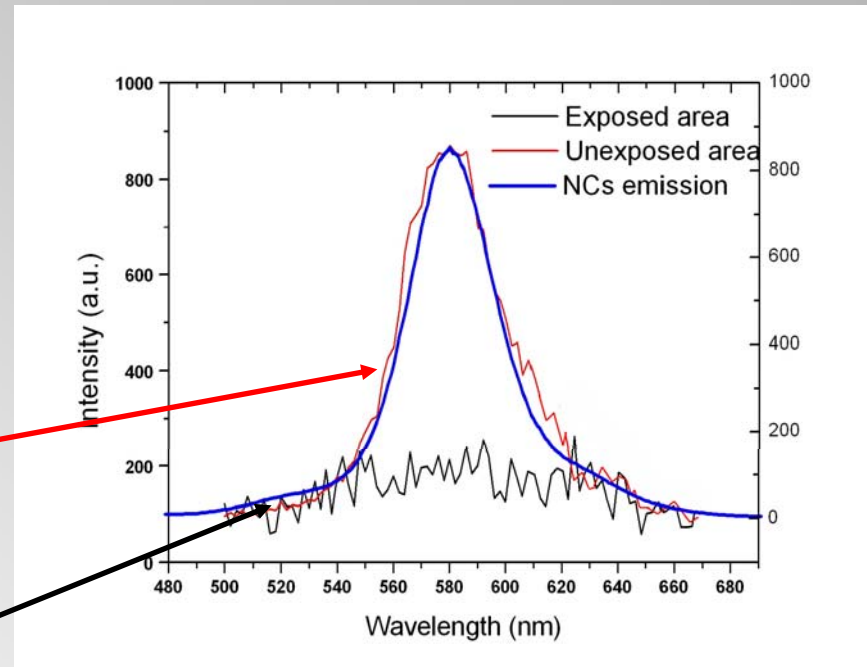
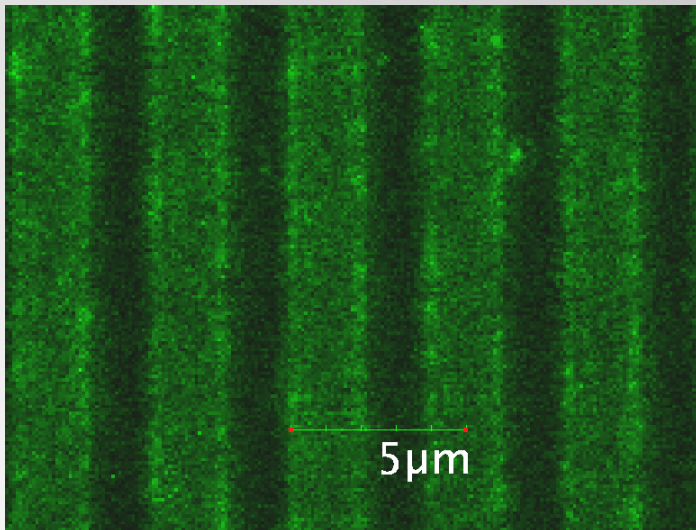


**The positive resist behaviour of PMMA is not perturbed
by the presence of NCs**

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



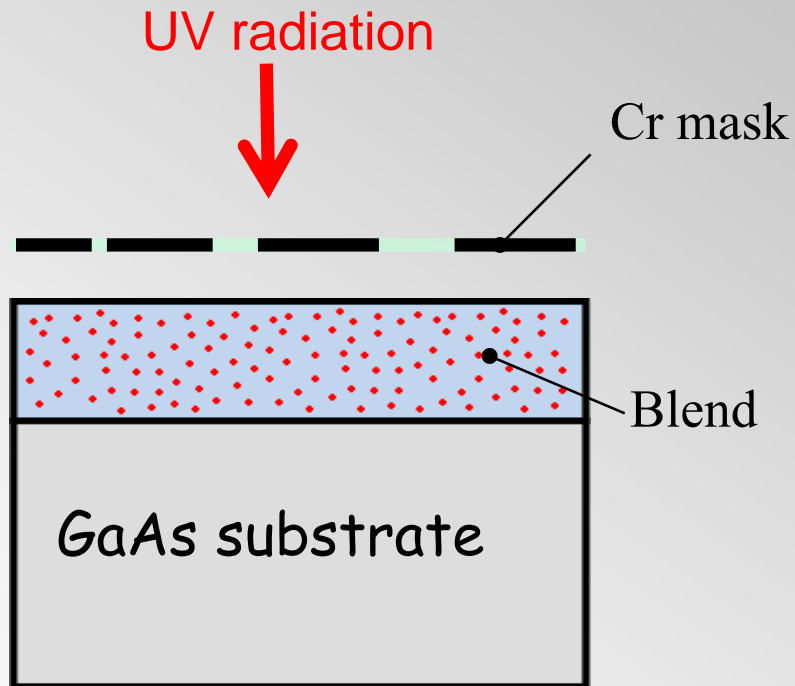
Photoluminescence maps by confocal microscope



PL signal is detected only in the unexposed regions

The emission spectrum of NCs is not affected by EBL

SU-8/NCs blend Optical Lithography

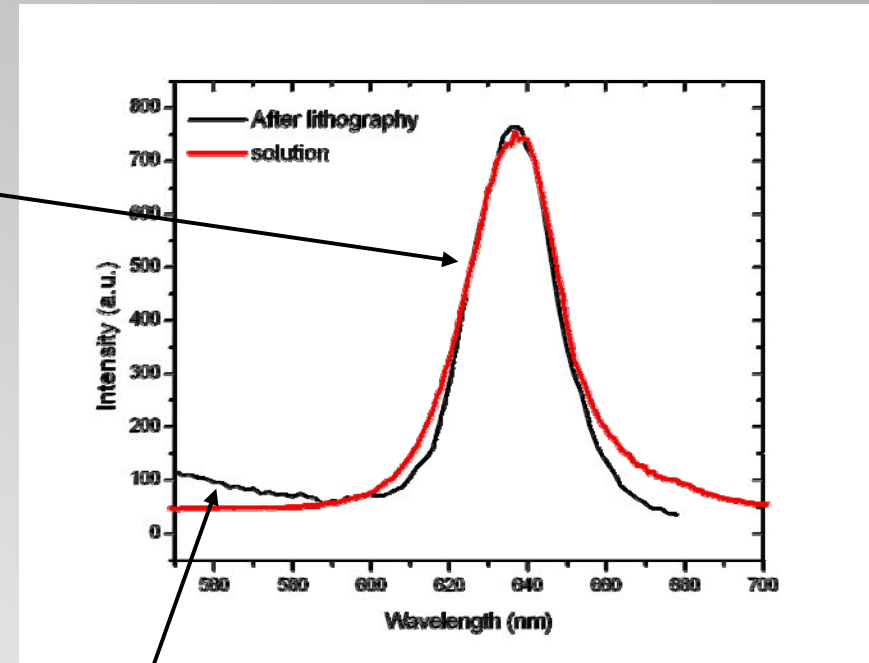
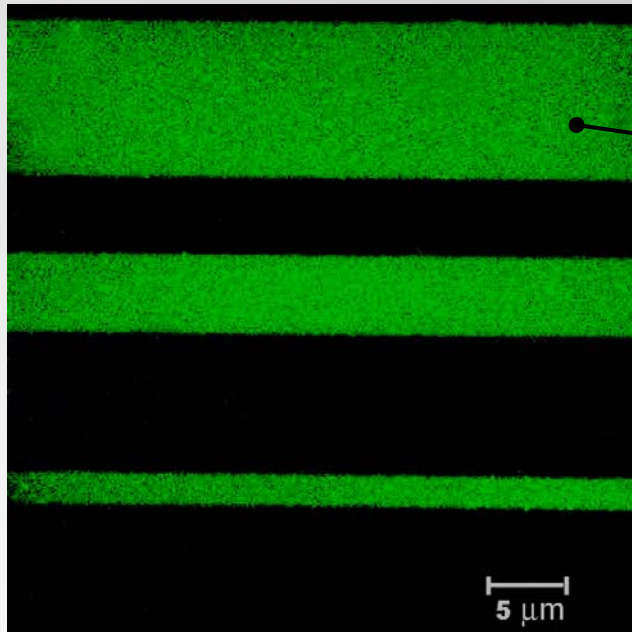


Stripes width: 2 – 100 μm

UV source: Hg i-line @ $\lambda=365$ nm

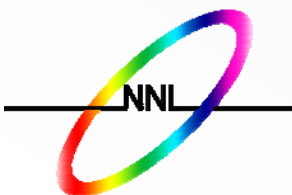


Photoluminescence maps by confocal microscope



SU-8 luminescence

PL signal is detected only in the exposed regions
The emission spectrum of NCs is not affected by UV

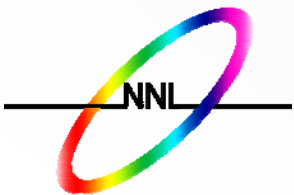


L. Martiradonna et al., *Physica Status Solidi B*, 243, 15, p.3972, 2006



NCs localization by lithographic techniques

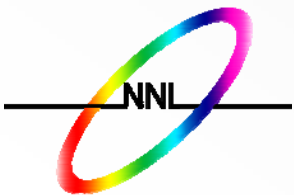
- **e-beam lithography and photolithography**
- **positive and negative resists**
- **optical properties of NCs not affected by exposure**
- **resolutions down to 20 nm achieved**
- **slight increases of exposure doses for positive resists**
- **for negative resists, exposure dose increase roughly proportional to the NCs concentration in the blend**



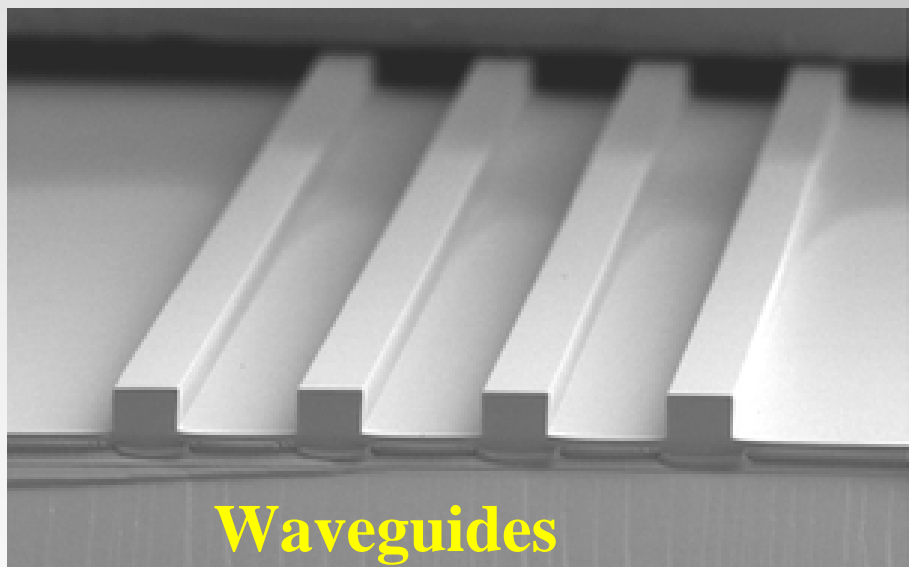
NCs localization by lithographic techniques

Several advantages:

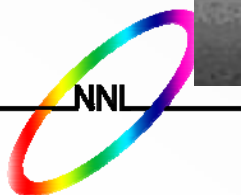
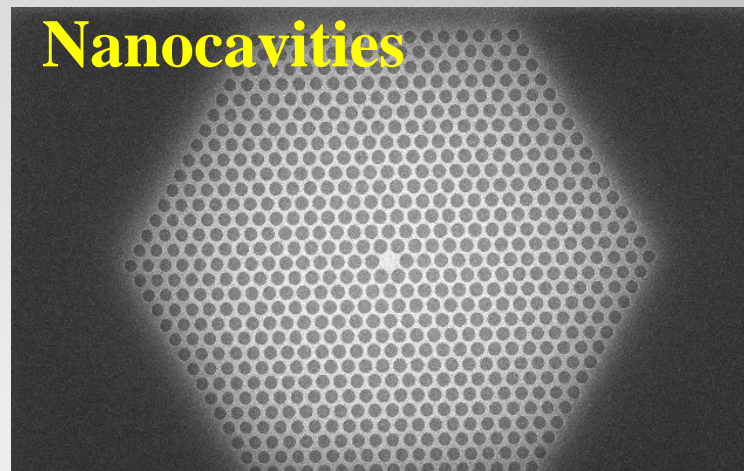
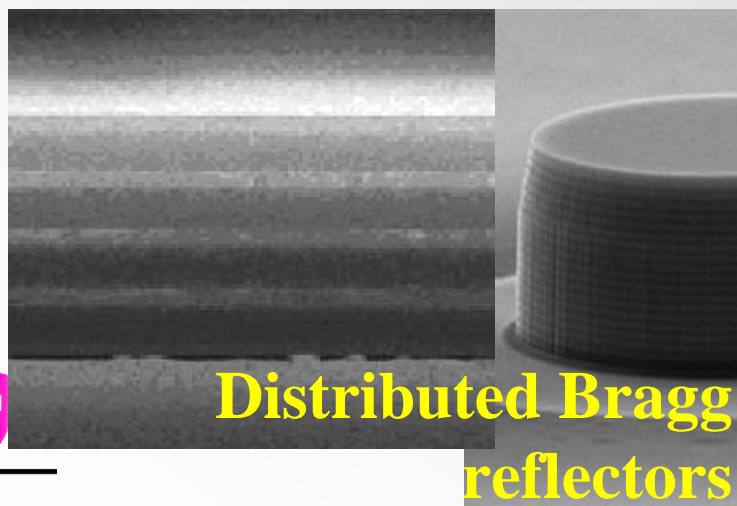
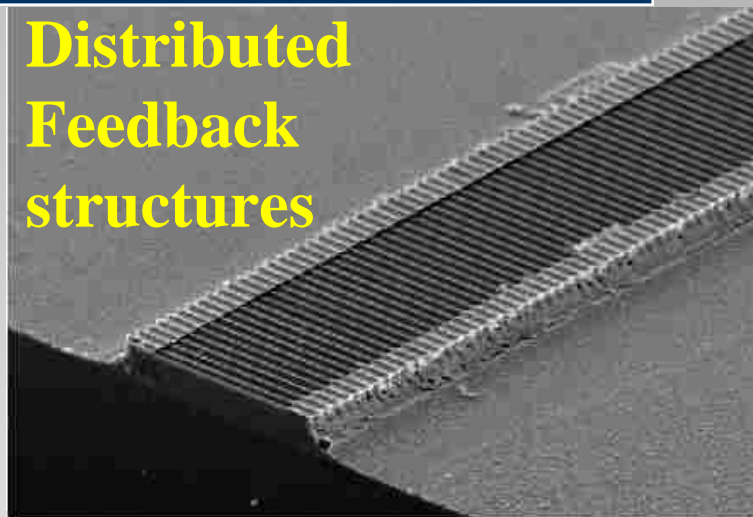
- any kind of substrate without recurring to chemical or physical treatment of the surfaces;**
- not only rigid substrates but also flexible devices;**
- the typical resolution is defined by the lithographic process;**
- the density of emitters can be easily tuned by varying the relative molar concentration of the two components (NCs – resist);**
- refractive index of the blend tunable with the NCs concentration.**



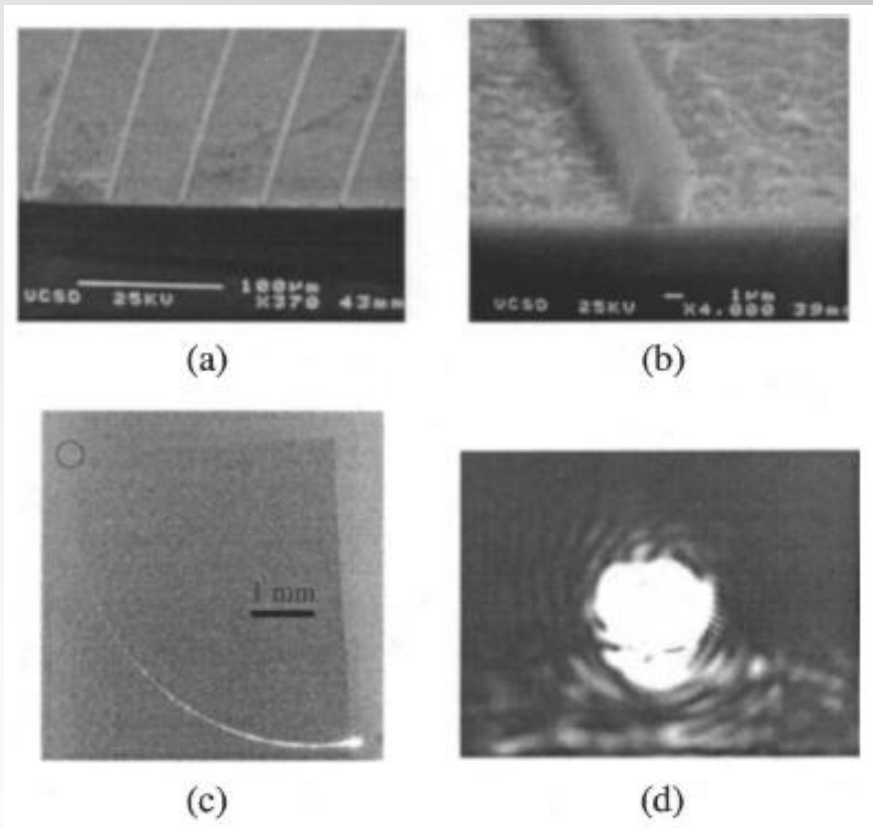
Building blocks for photonic devices



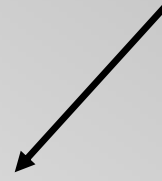
Distributed Feedback structures



Building blocks for photonic devices

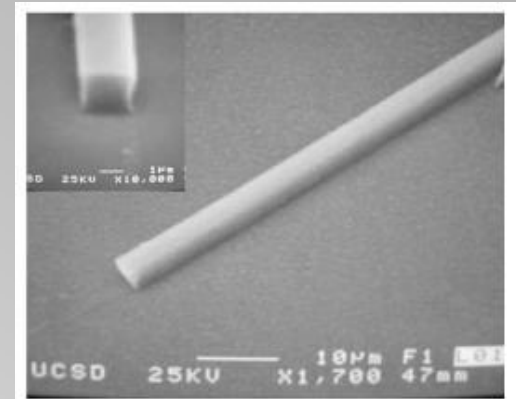


PMMA/NCs

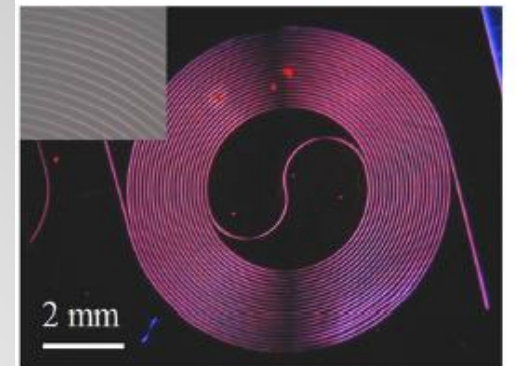


Waveguides

SU-8/NCs



(a)



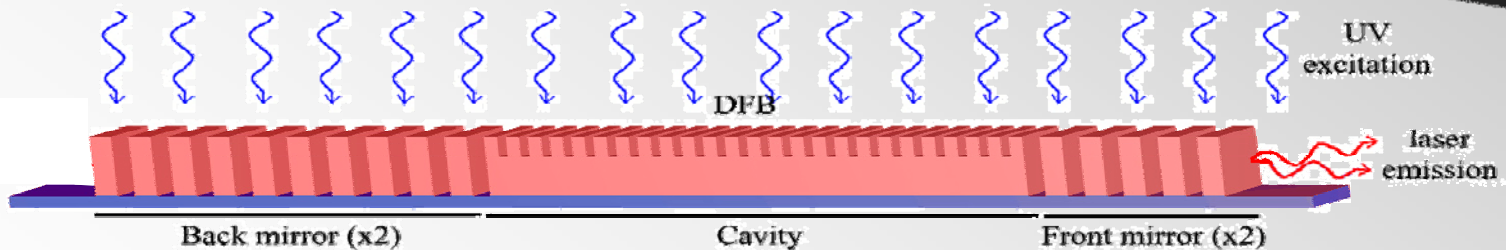
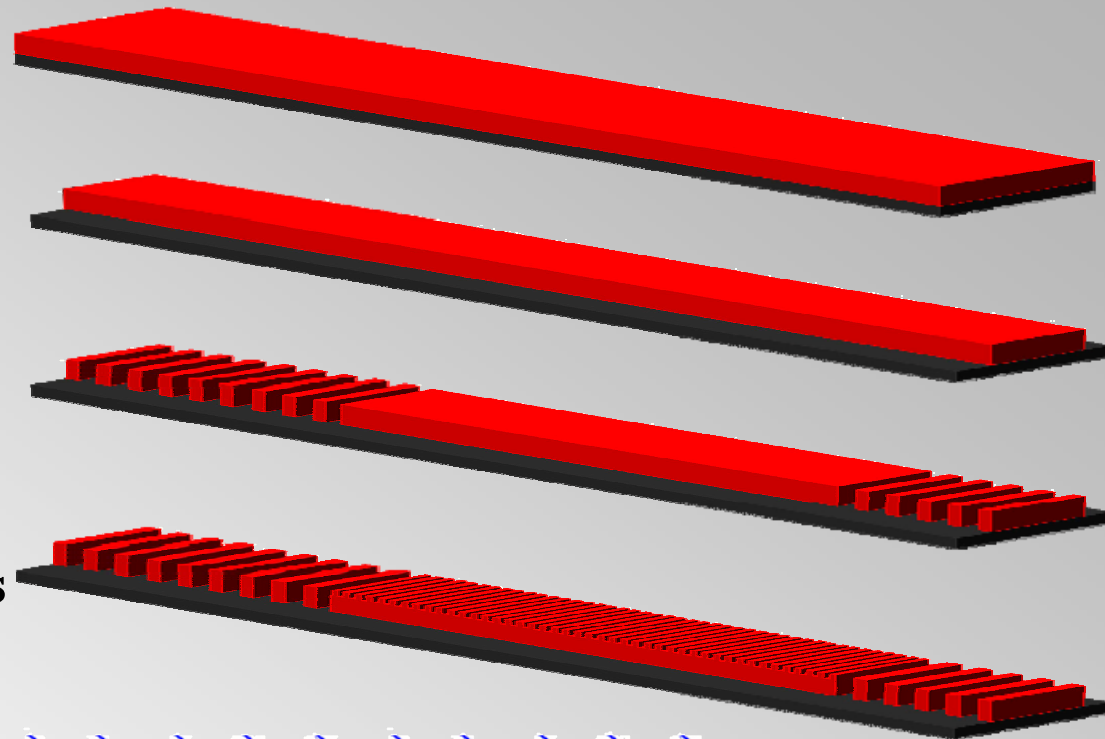
(b)

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

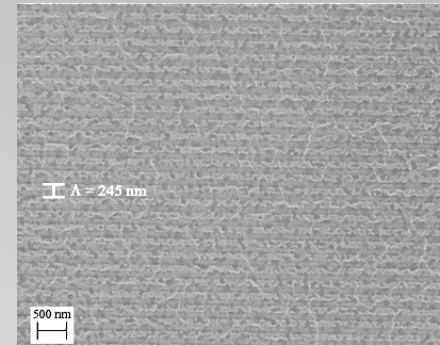
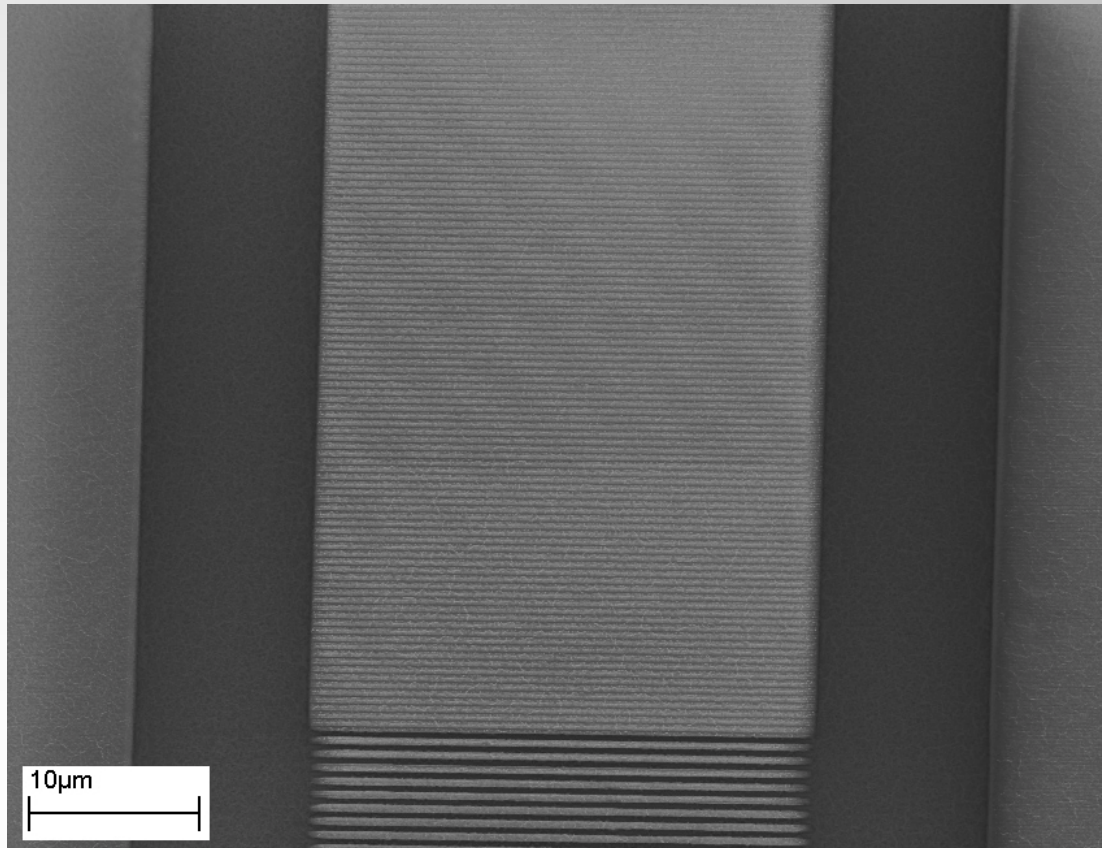


Building blocks for photonic devices

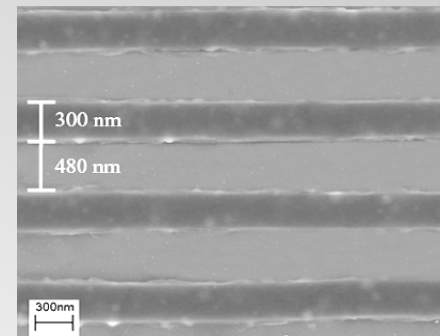
- Uniform resist/NCs layer
- Ridge waveguides
- Distributed Bragg Reflectors (DBRs)
- distributed feedback (DFB) structures



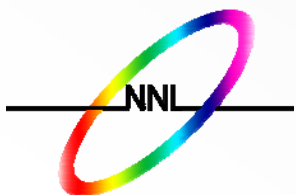
Building blocks for photonic devices



DFB
 $L_{\text{BRAGG}} = 245 \text{ nm}$
 $\text{thk} = 40 \text{ nm}$



DBR
 $3\lambda/4$ stripes
 $\text{thk} = 400 \text{ nm}$



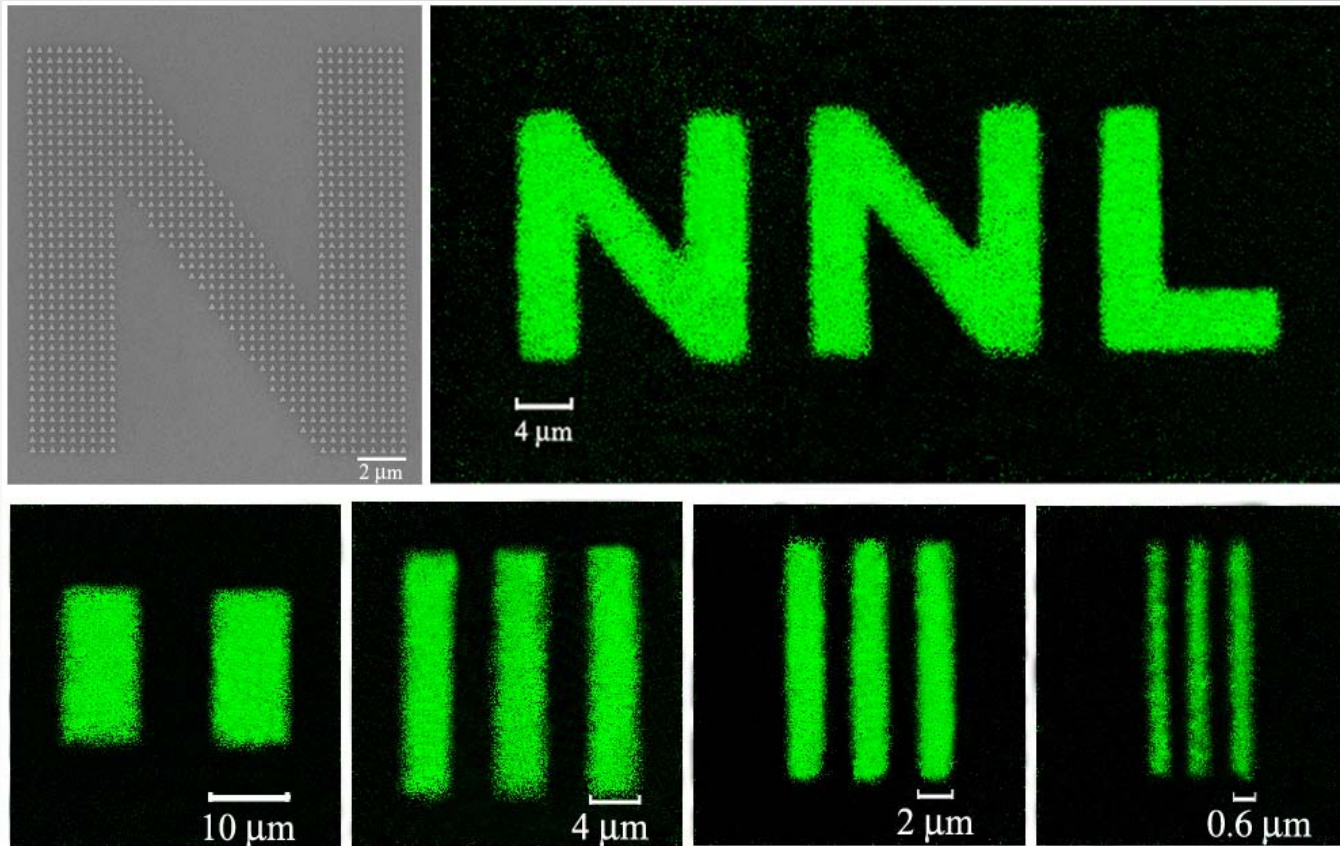
L. Martiradonna et al., *Sens. Actuators B: Chem* 126, p.116 (2007)



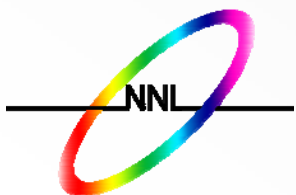
And more...



Enhancement of NCs luminescence by coupling with surface plasmons



- Metallic nanopatterns defined by EBL; NCs/PMMA blends spin-coated on top
- Good control of the coupling between surface plasmons and colloidal nanocrystals
- Enhancement of the NCs emission with nanoscale control

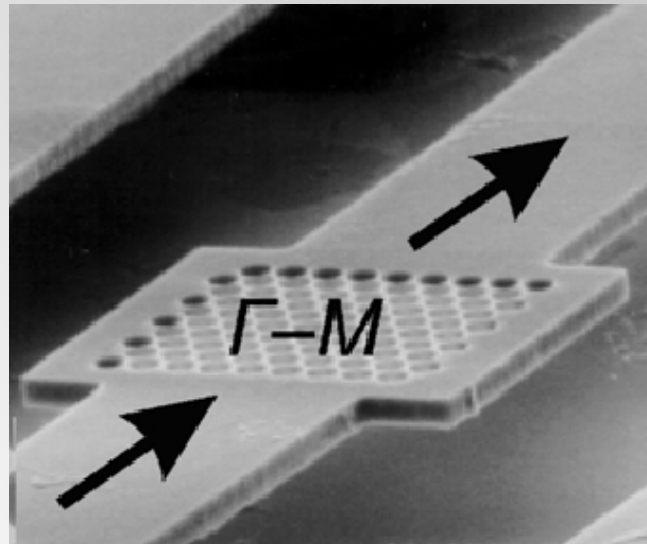


P.P. Pompa, L. Martiradonna et al., Nature Nanotechnology 1, p.126 (2006)

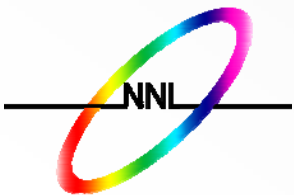


Low index contrasts → Suspended structures

- NCs in polymeric blend increase the refractive index but:
 - maximum $\Delta n \sim 0.3$
 - maximum $n_{\text{blend}} \sim 2$
- Substrates with low refractive indices : SiO_2 , glasses ($n \sim 1.5$)
 - air is better ($n \sim 1$)

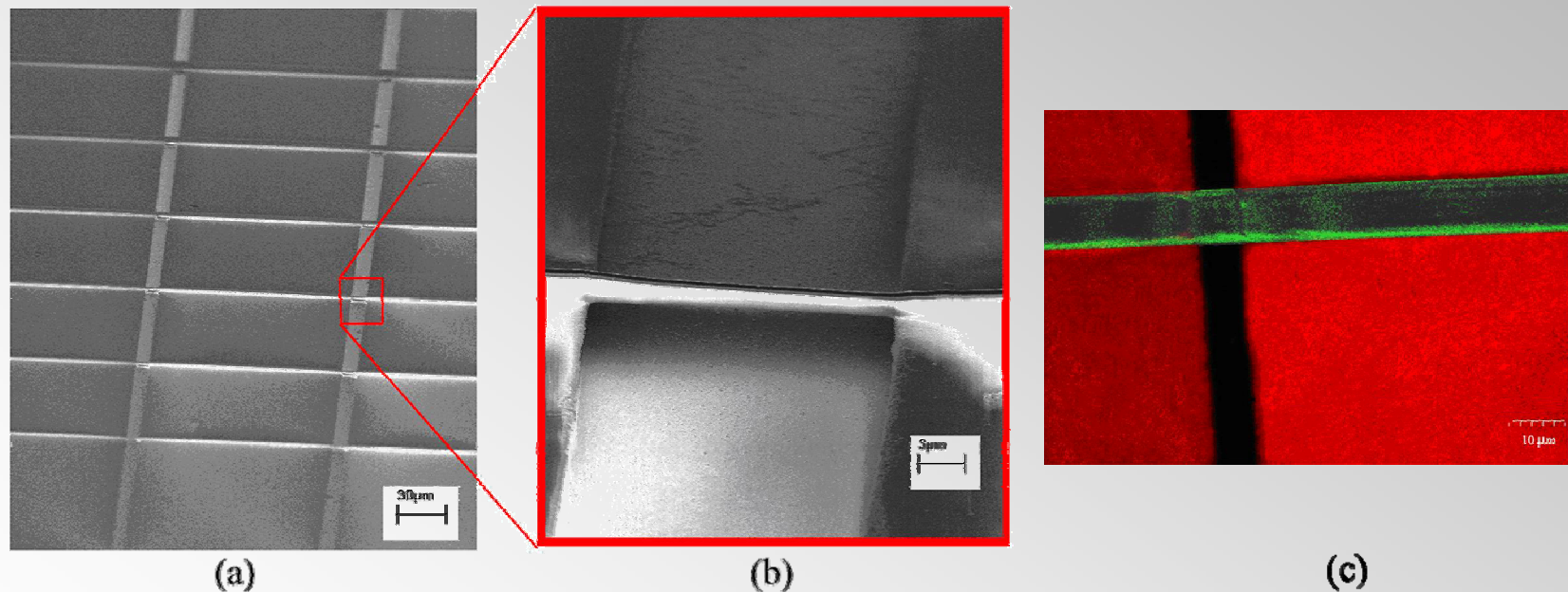


Air-bridge
devices



Low index contrasts → Suspended structures

- 1st lithography: SU-8/red NCs (thickness: 1500 nm, grooves width: 2 – 30 μm)
- 2nd lithography: SU-8/green NCs (thickness: 1500 nm, stripes width: 2 – 100 μm)
- single development after both exposures



-Suspended NC/resist waveguides with all-lithographic steps

- No residual NCs layers



A. Quattieri et al., *Microelectron. Eng.*, 84, 5-8, p.1488, 2007.



Conclusions and further developments

- **Localization of resist/NCs blends by lithographic techniques is a suitable approach for the fabrication of photonic devices with nanometer resolution**
- **Fabrication of the main building blocks of a photonic device: waveguides, DBRs, DFB**
- **Possibility to increase the NCs luminescence by coupling with surface plasmons**
- **All-lithographic approach for the fabrication of air-bridge structures**
- **Possibile use of flexible substrates**
- **No-phase separation observed in blends with high molar concentrations of NCs**
- **To be checked: conditions for Amplified Spontaneous Emission in resist/NCs blends → lasers fabrication**



Aknowledgments

- **Dr. Liberato Manna, Luigi Carbone (NNL – Universita' del Salento)**
- **Gianmichele Epifani, Benedetta Antonazzo (NNL – Universita' del Salento)**
- **Prof. Arakawa and Arakawa lab members (IIS – University of Tokyo)**

