Photoluminescence Spectroscopy on Chemically Synthesized Nanoparticles

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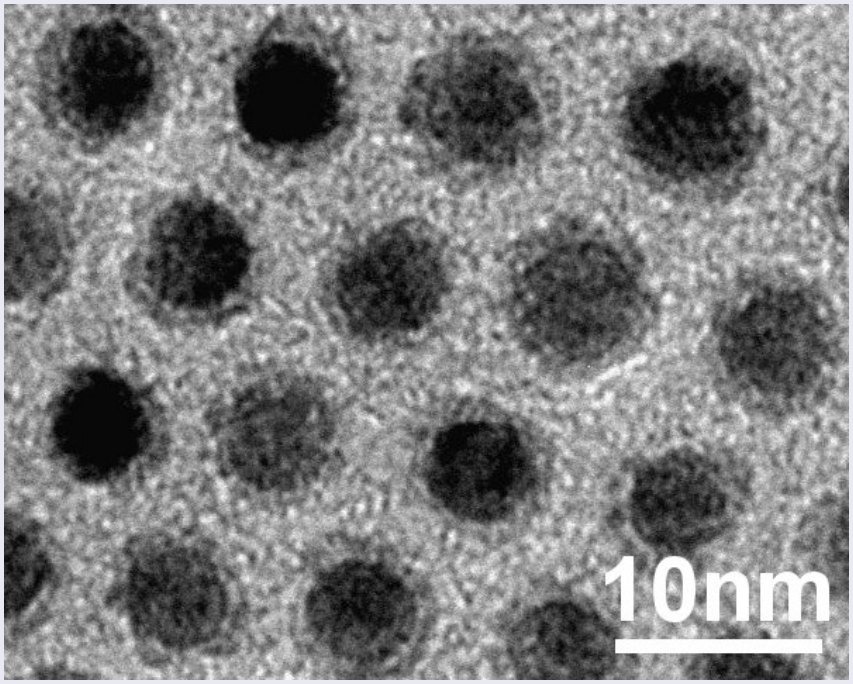
Universität Hamburg

Diploma Talk, 18.12.2007

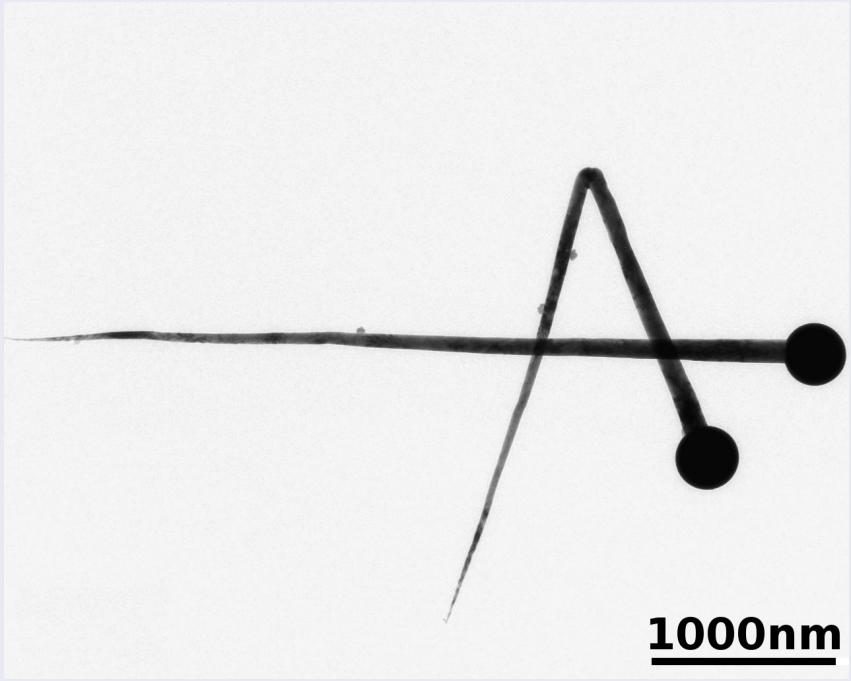
[1] http://www.entorb.net

Contents

Nanocrystals



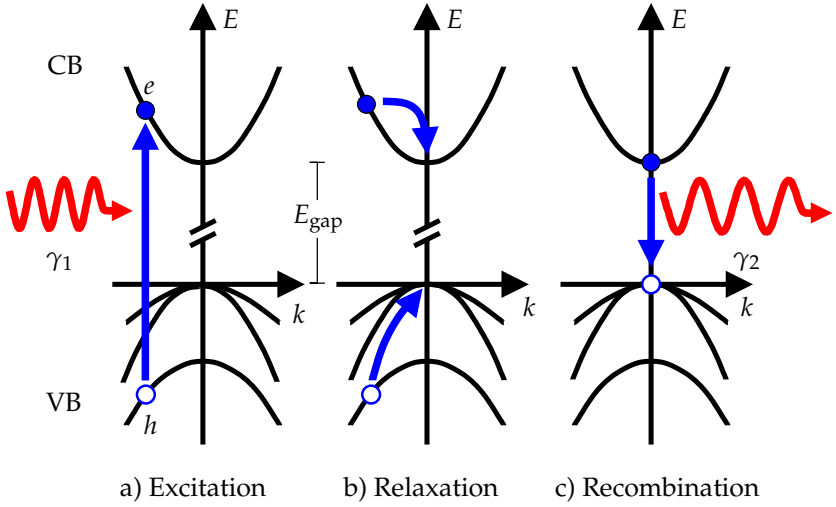
Nanoneedles



Images by Weller-Group, HH

Photoluminescence (PL)

PL-schema for semiconductors with direct bandgap:



a. **Excitation**
absorption of photon γ_1 generates *e*-*h*-pair

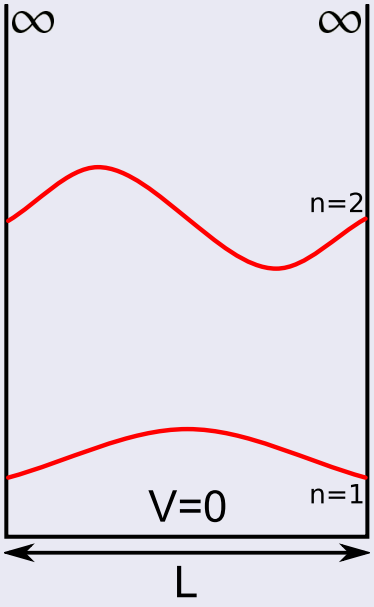
b. **Relaxation**
e and *h* interact with the lattice until they reach the band extrema

c. **Recombination**
only effective path to the ground state is recombination
$\rightarrow$ photon γ_2 is emitted

Confinement

- nanometer-scaled semiconductors show increased bandgap
- increasing impact of material borders as size is decreased

simple 1D ansatz: ∞-boxpotential



$$n \cdot \frac{\lambda}{2} = L; \quad k = \frac{2\pi}{\lambda}; \quad E = \frac{\hbar^2 k^2}{2m}$$

$$\Rightarrow E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$

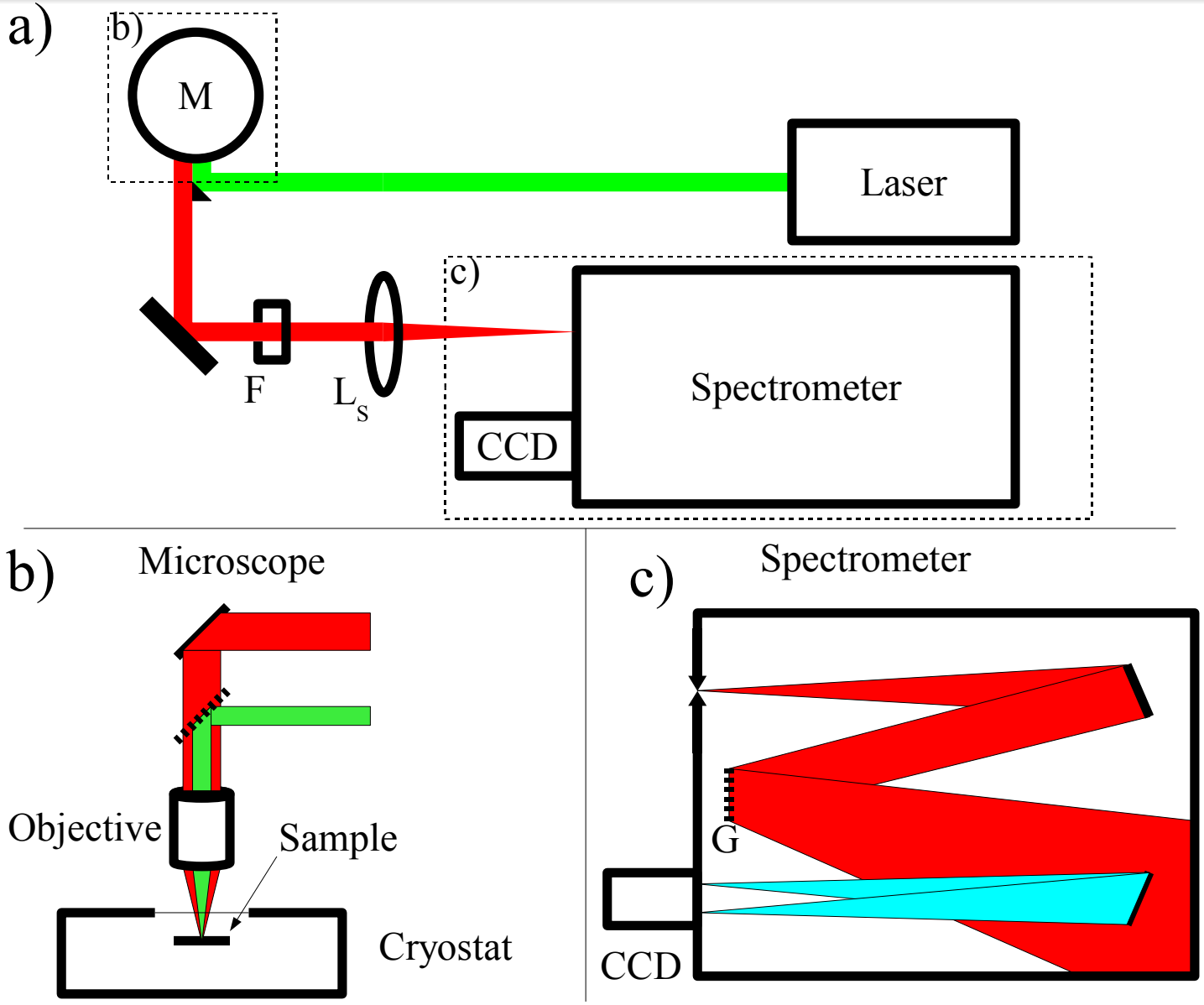
$$E_{\text{gap,Conf.}} = E_{\text{gap,bulk}} + E_n$$

bandgap directly tunable via size L

PL of Nanocrystals

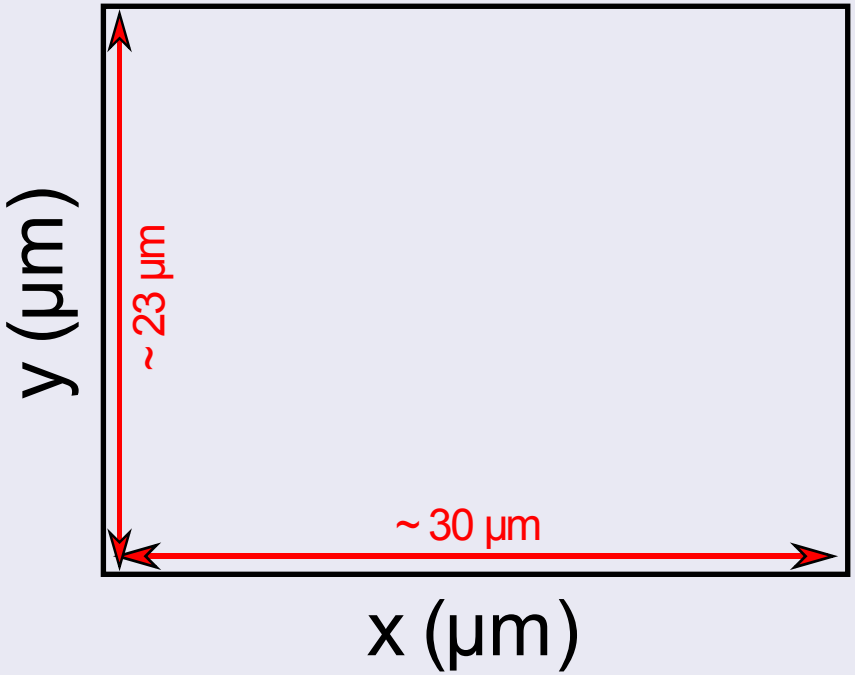
Image by Weller-Group, HH

Setup

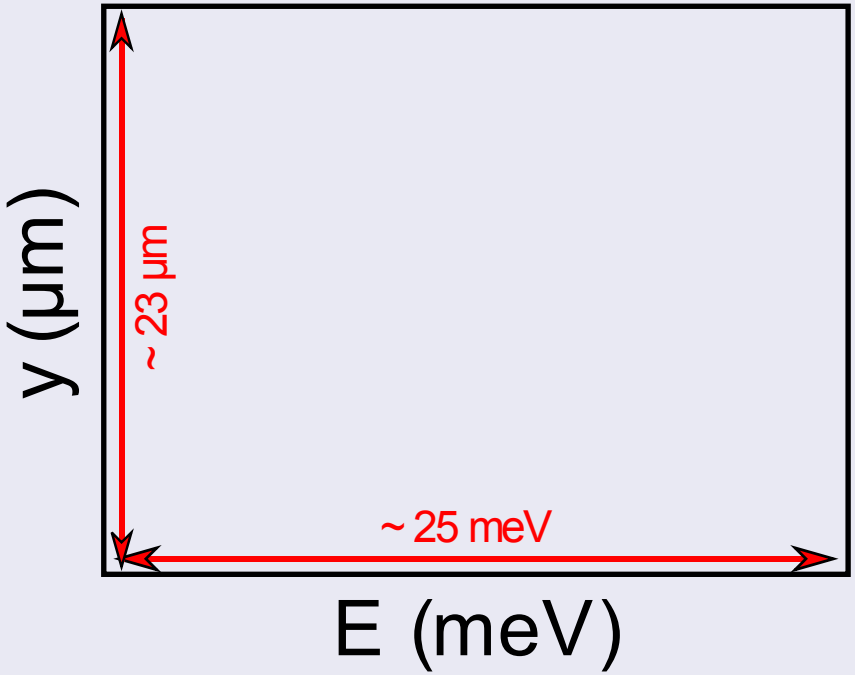

a)
b)
M
Laser
c)
F
L_s
Spectrometer
CCD
b)
Microscope
Objective
Sample
Cryostat
c)
Spectrometer
G
CCD

CCD-Detector

Spacial mode



Spectral mode



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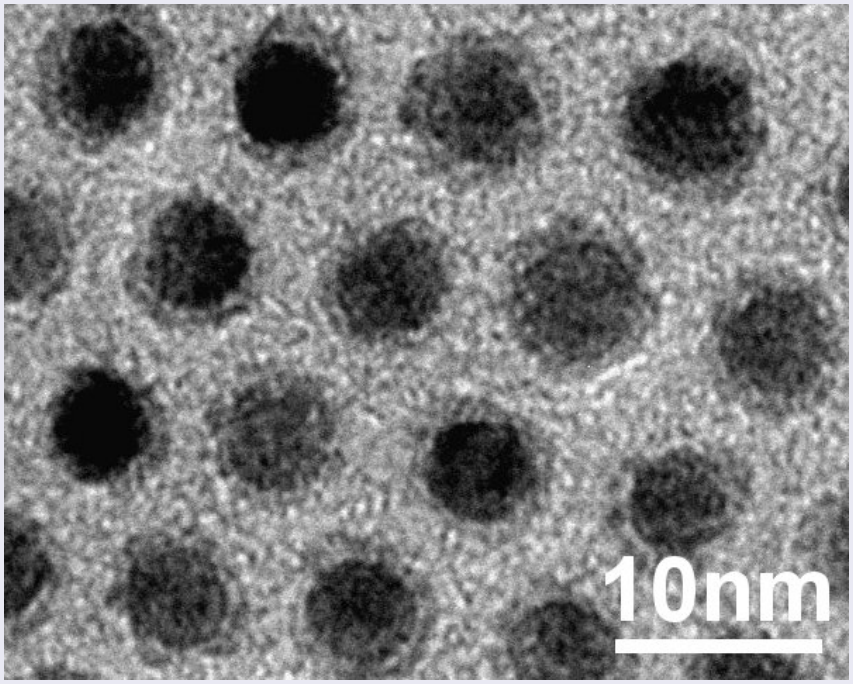

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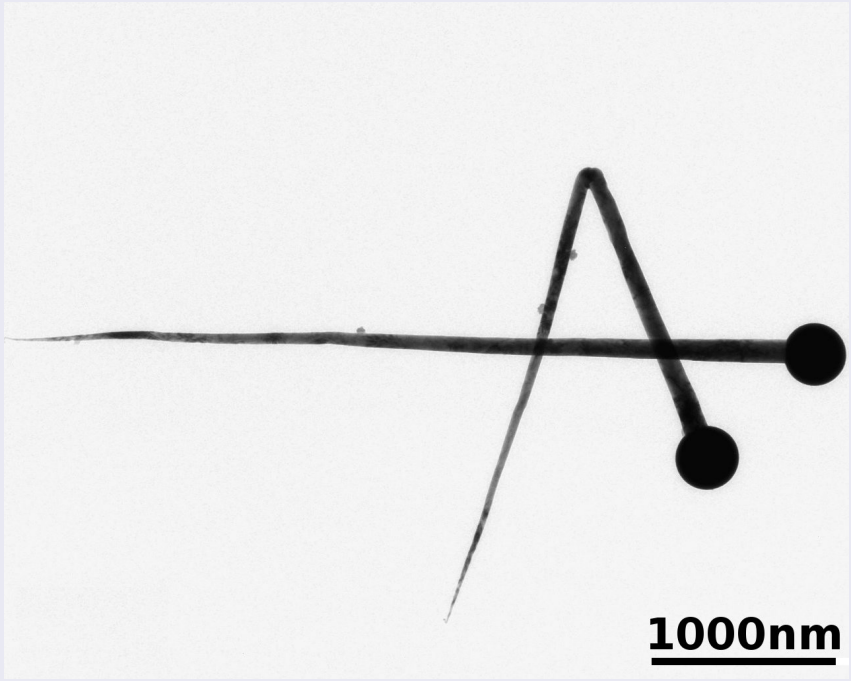

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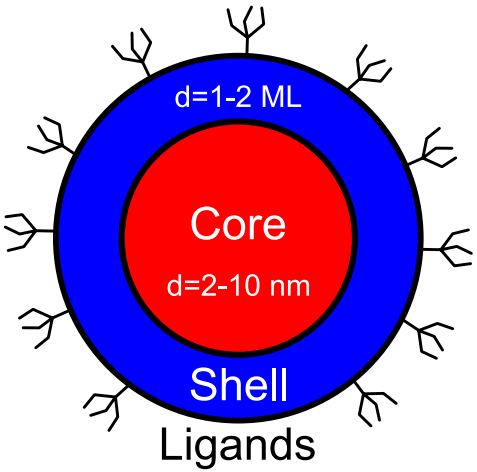
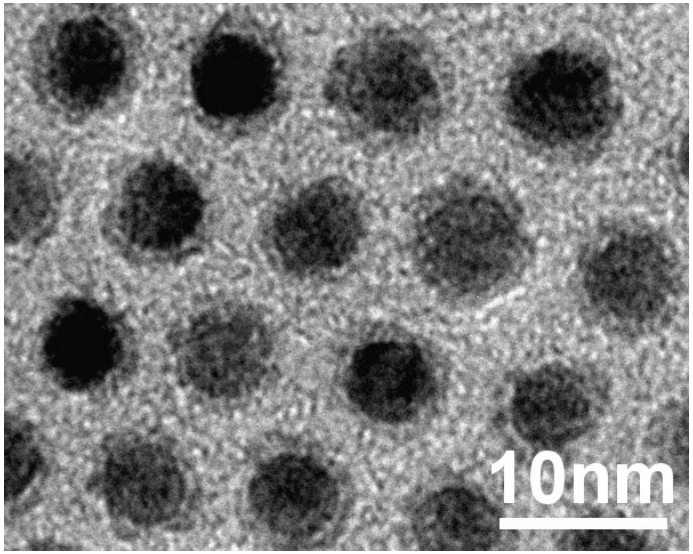
Structure

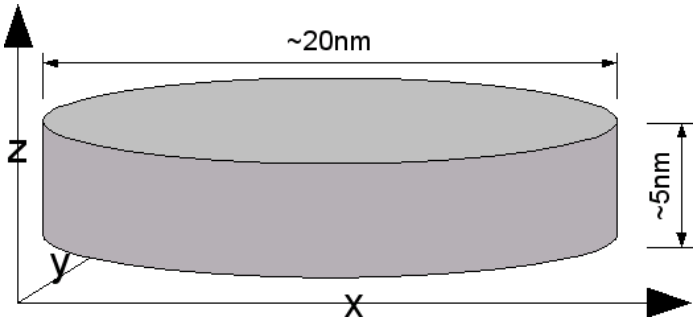




- spherical particle
- wet chemical synthesis
- ligands slow down growth process, prevent agglomerate-building and passivate surface
- “core” of ≈ 2-10 nm
- often surrounded by one or two “shells”
- spin-, dip- or drop-coating onto substrate

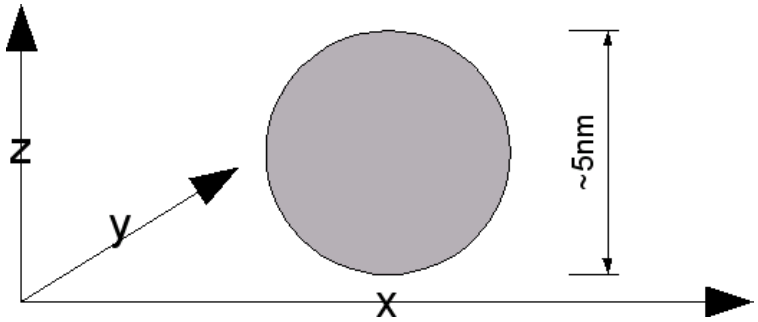
MBE-Grown Quantum Dots vs. Nanocrystals

Quantum Dot



elliptical shape ⇒ strongest confinement in growth direction

Nanocrystal



spherical geometry same confinement in all 3 directions

Advantages

embedded growth in other structures (cavities. . .)

industrial synthesis possible

Applications

LEDs, photovoltaic cells, biomonitoring, interactions with cavities

First Tasks

- transport experiment to a lab of higher spectral resolution
- investigate ensemble and single NCs
- get more information of PL-signal of single NCs
- verify results Gerwin Chilla found in the another lab

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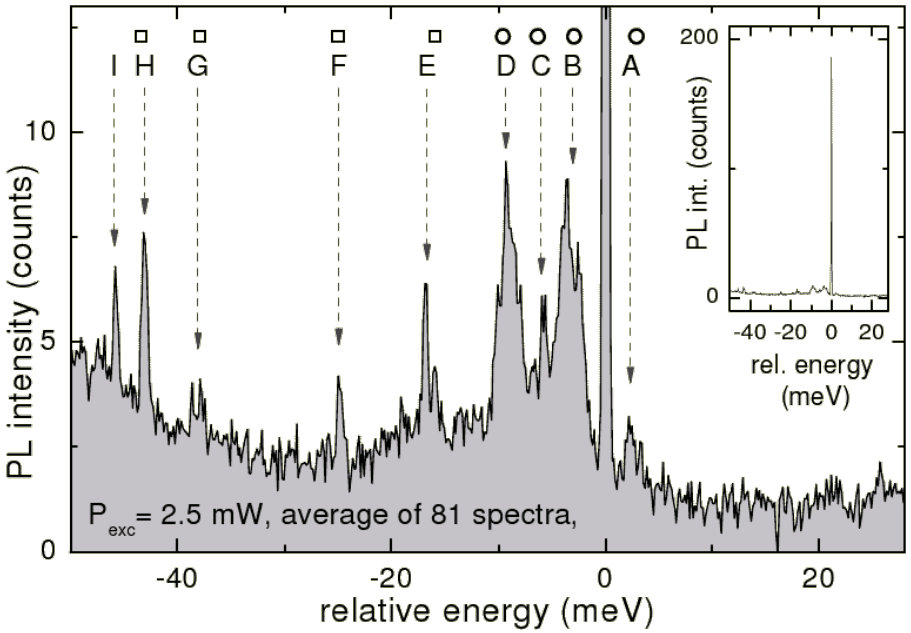
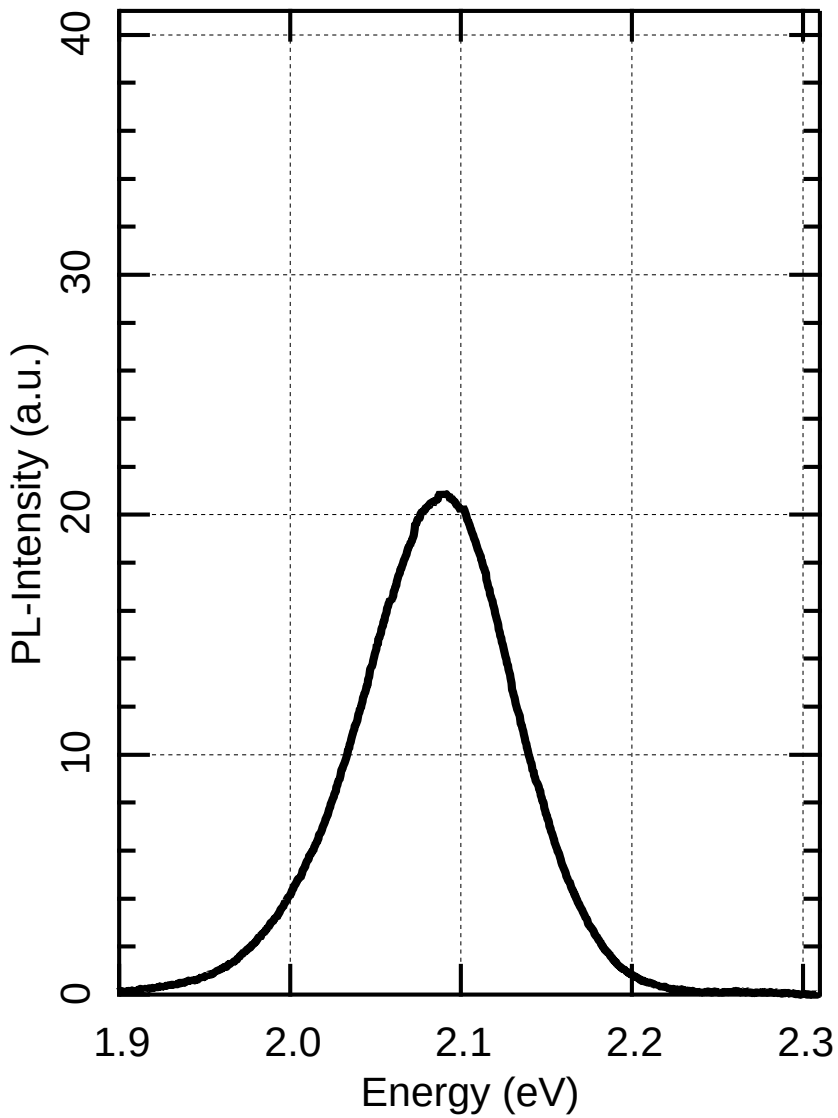
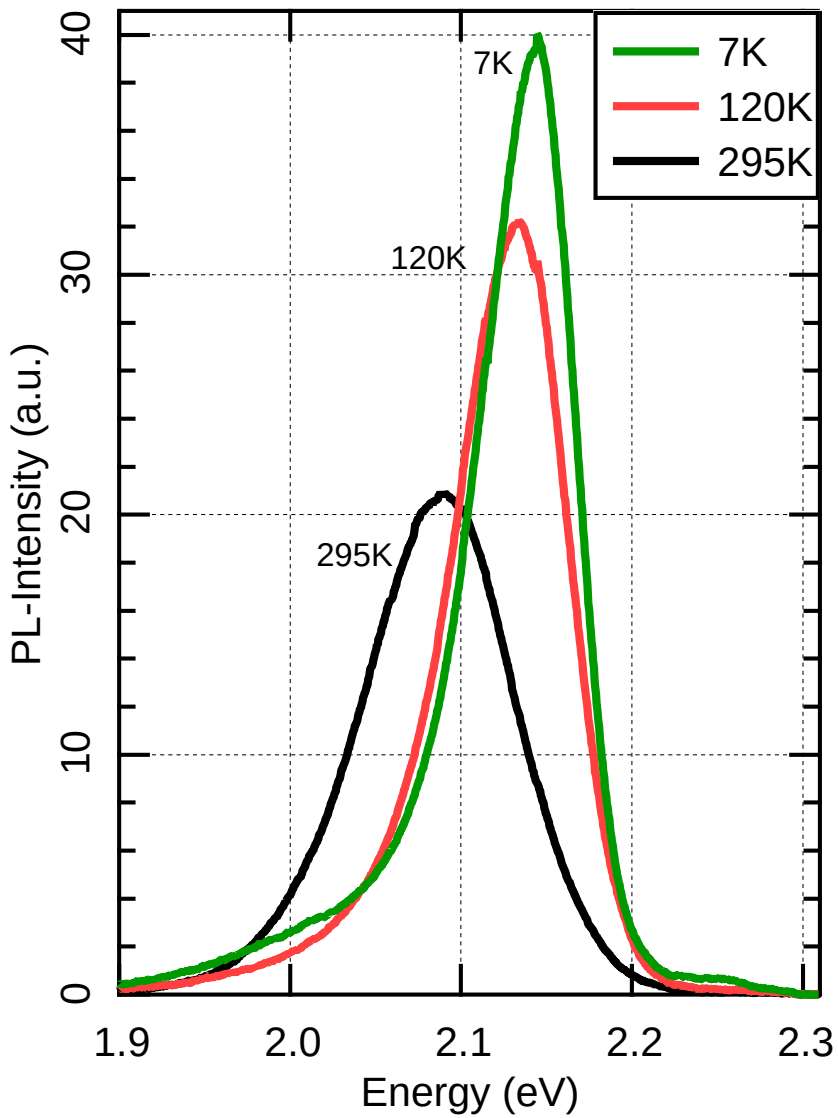


Ensemble Measurements on CdSe-NCs



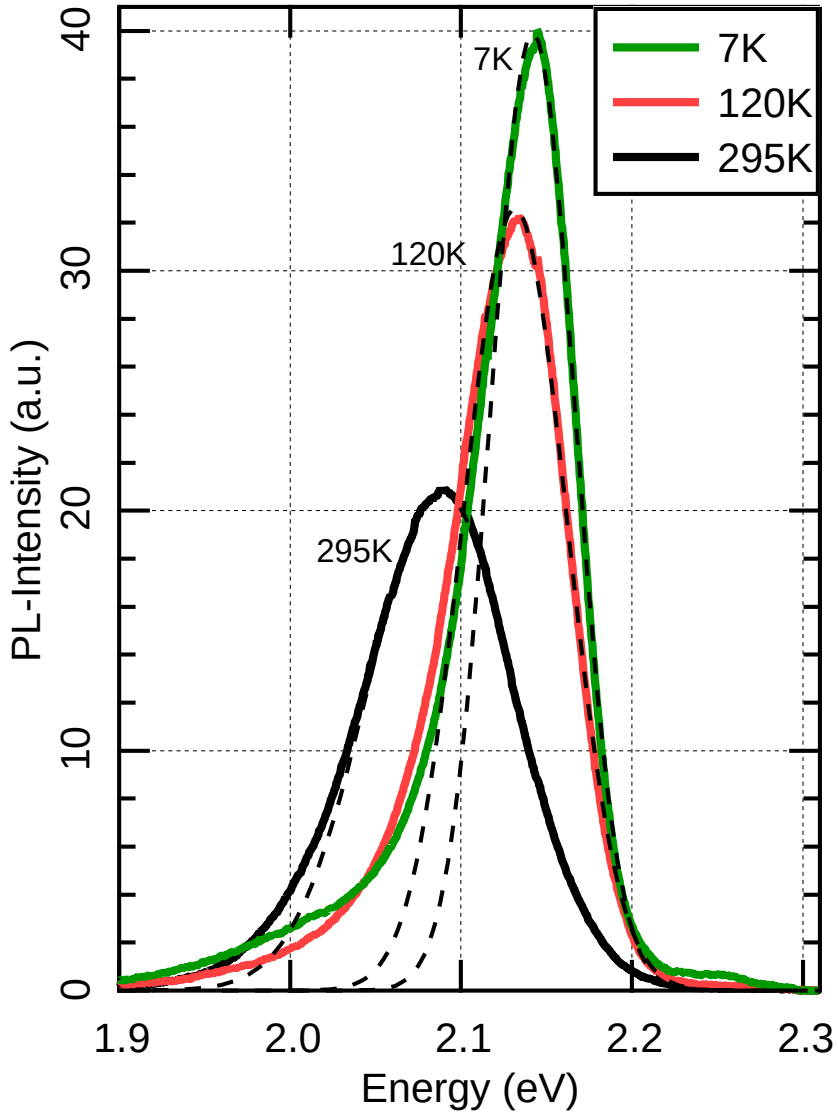
- gaussian-shape
- peak energy high above bulk band gap (1.751 eV at 293 K) ⇒ *confinement*

Ensemble Measurements on CdSe-NCs



- gaussian-shape
- peak energy high above bulk band gap (1.751 eV at 293 K) ⇒ *confinement*
- blueshift ⇒ *increased bandgap*
- decreasing peak width ⇒ *less interactions with phonons*
- 2-fold increased signal ⇒ *less non-radiative recombination channels*

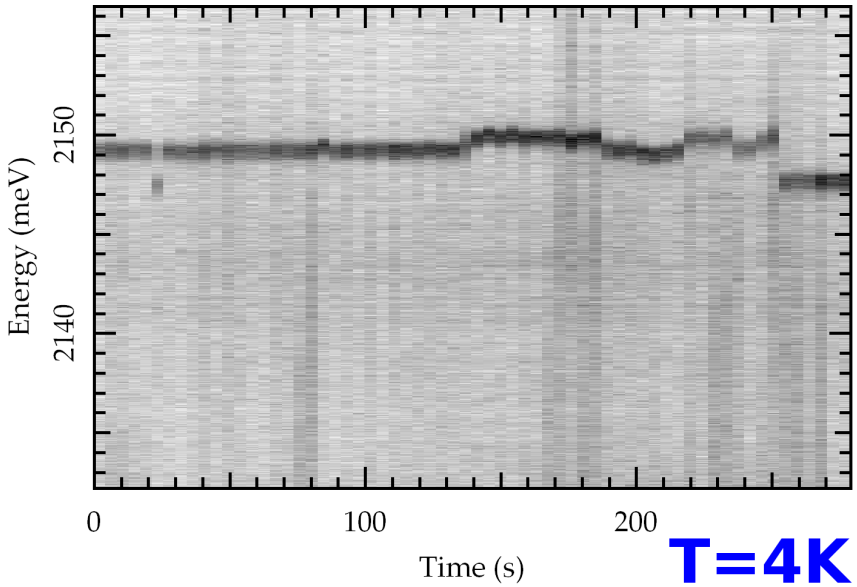
Resonance Energy Transfer



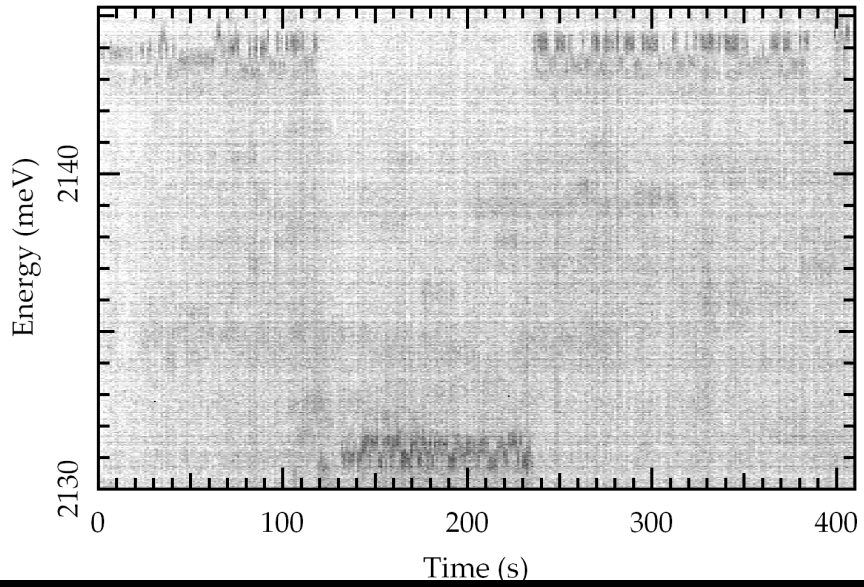
- deviation from gaussian-shape
- high-band-gap NCs pump low-band-gap NCs

⇒ *Förster Resonance Energy Transfer (FRET)*

PL of Single CdSe NCs



T=4K



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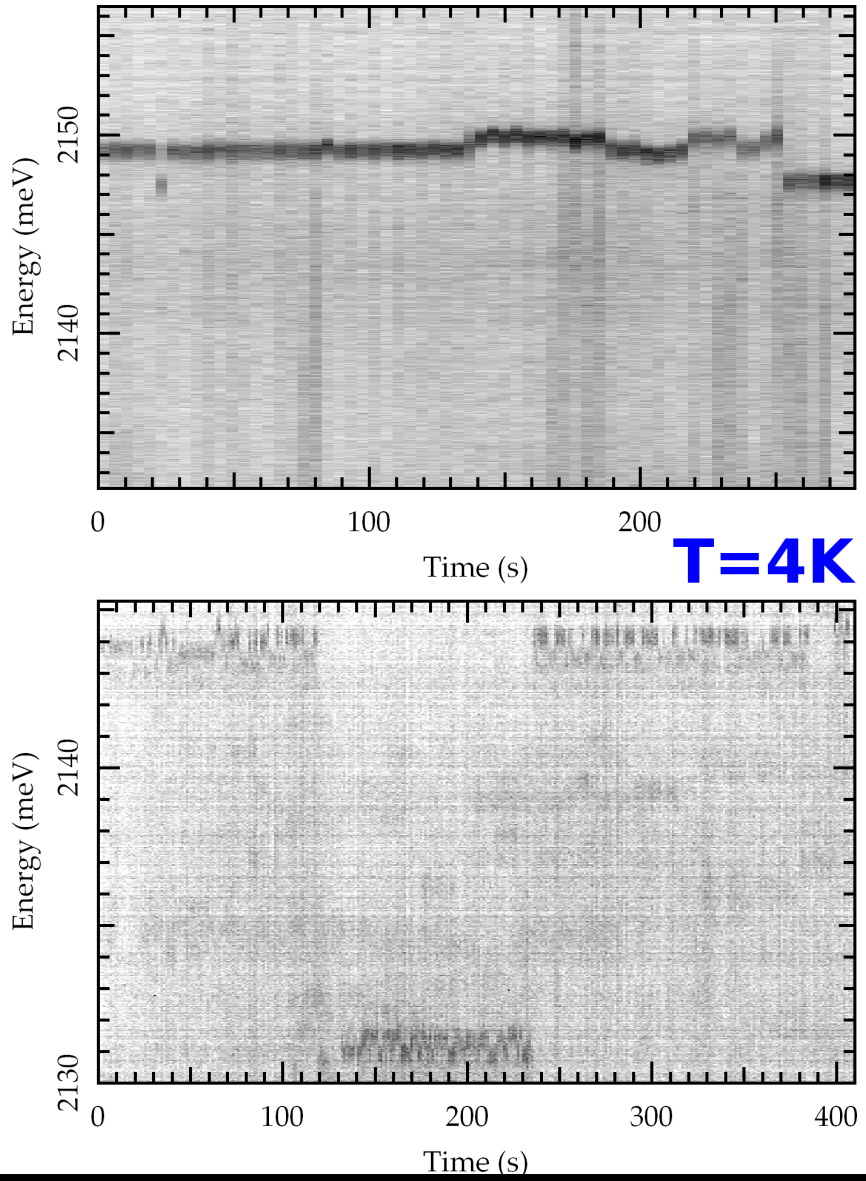
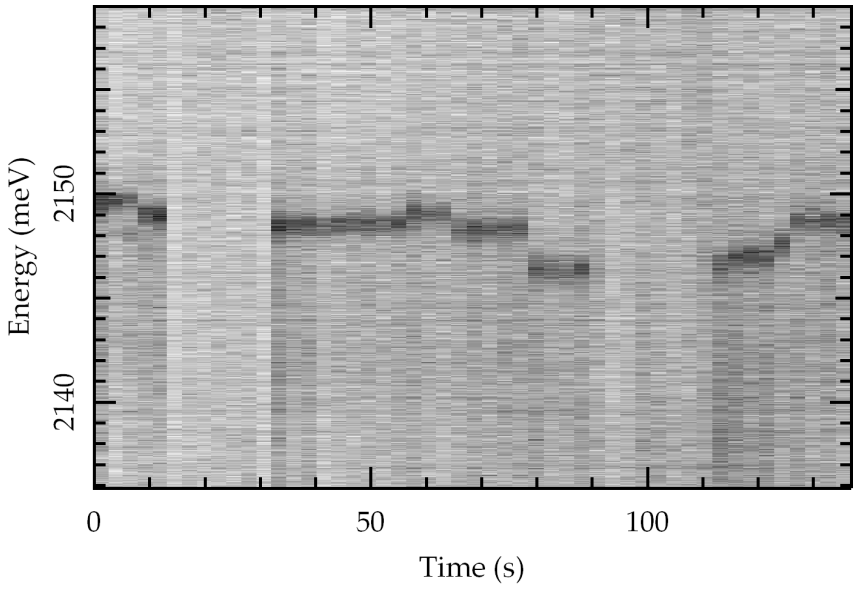
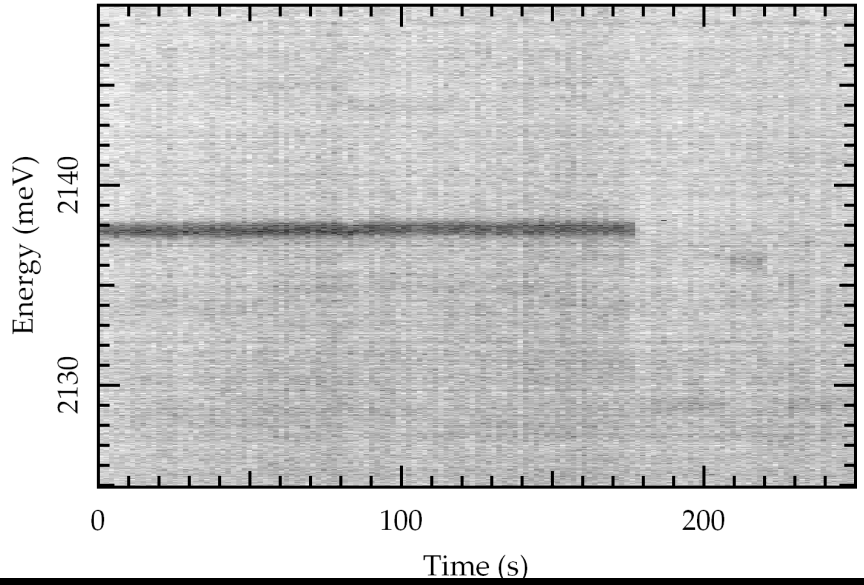


Shifting

shift of the PL-energy
can be explained by a change
of the potential in the
surrounding of the NC
→ *Stark-effect*

PL of Single CdSe NCs 2





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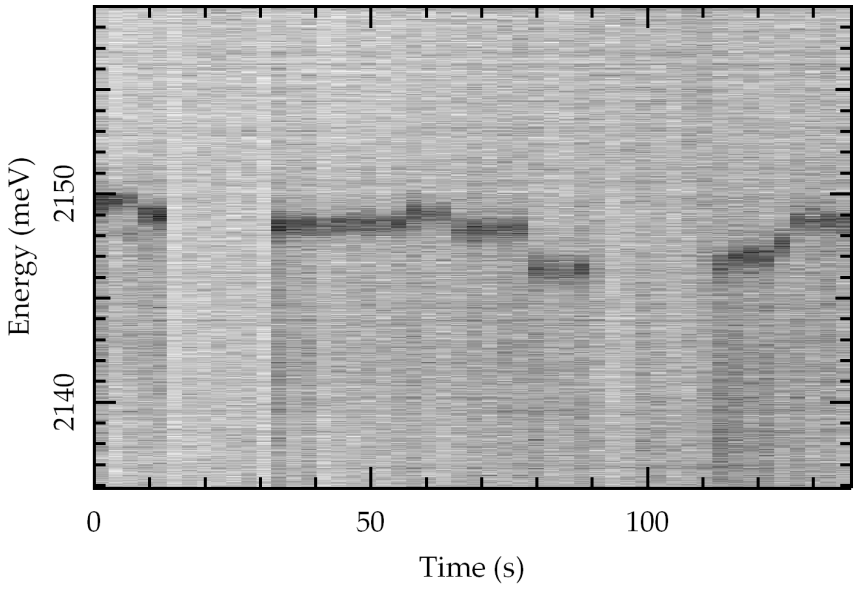
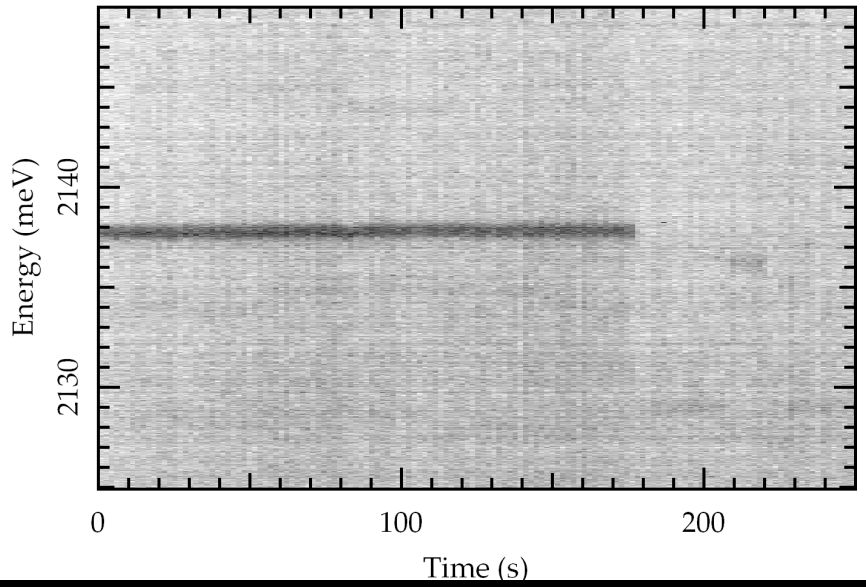




Blinking

no PL-signal for some of time (called *dark state*)
can be explained by ionization of the NC
→ *Auger recombination*

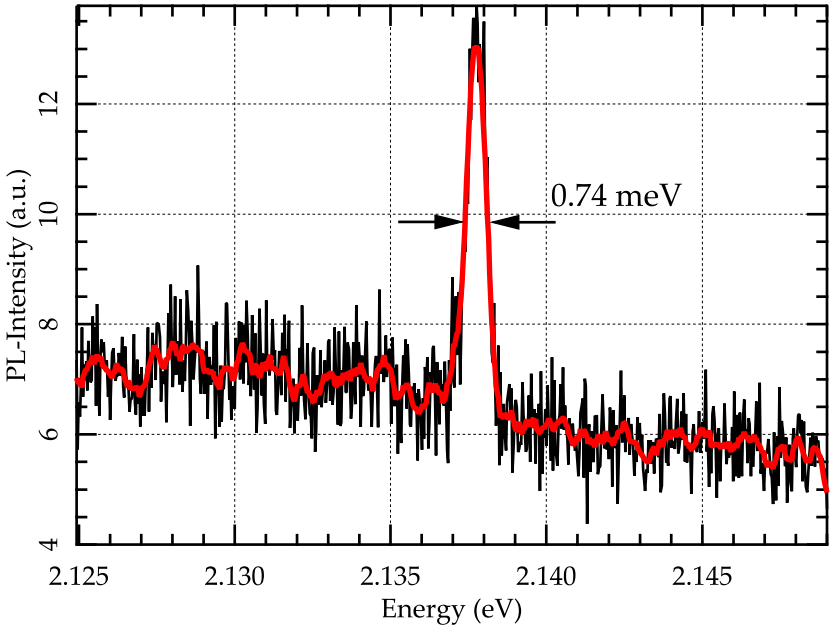
Auger Recombination

Auger Recombination

assumption: dark states caused by “charge-separation”

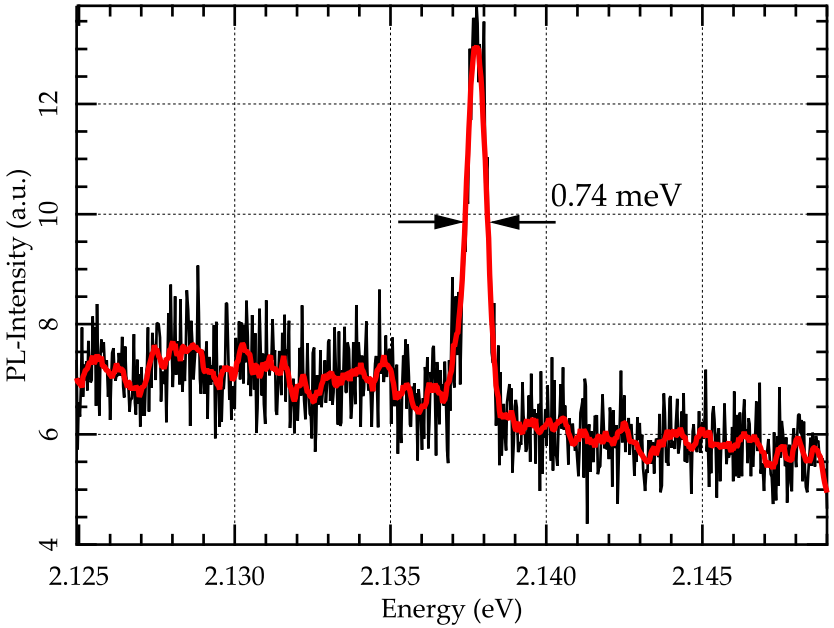
- generation of exciton (e-h-pair)
- one charge trapped by the surrounding ⇒ NC is “charged”
- photoexcitation of second e-h pair still allowed. . .
- . . . but their recombination energy is more efficiently transfered to the additional charge already present
- when the trapped charge is release the PL-signal is recovered

Single Nanocrystal



- 101 single spectra summed up
- aim: find fine-structure of PL-signal
- signal-to-noise ratio is too low

Single Nanocrystal



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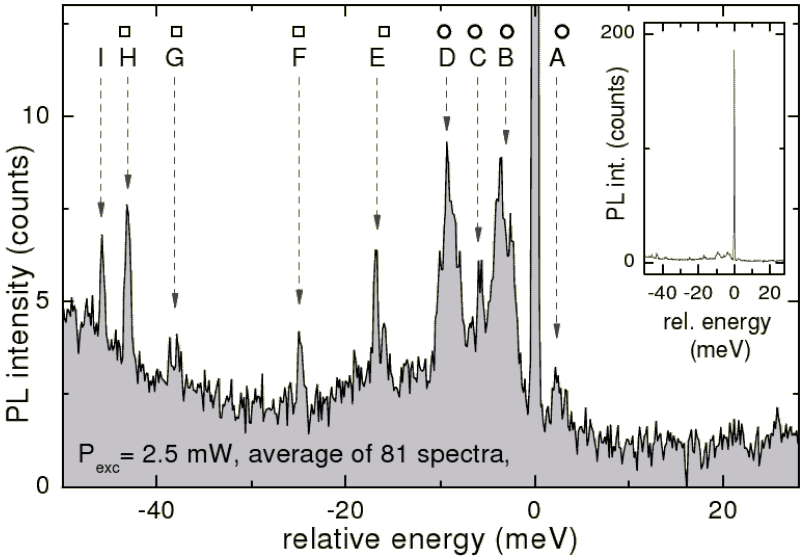

G. Chilla et al., PRL **100**, 057403 (2008)

NiPt/CdSe-Nanocrystals

Cooperation between Group K and Weller Group:

Is it possible to combine magnetic nanocrystals with an optic-active shell?

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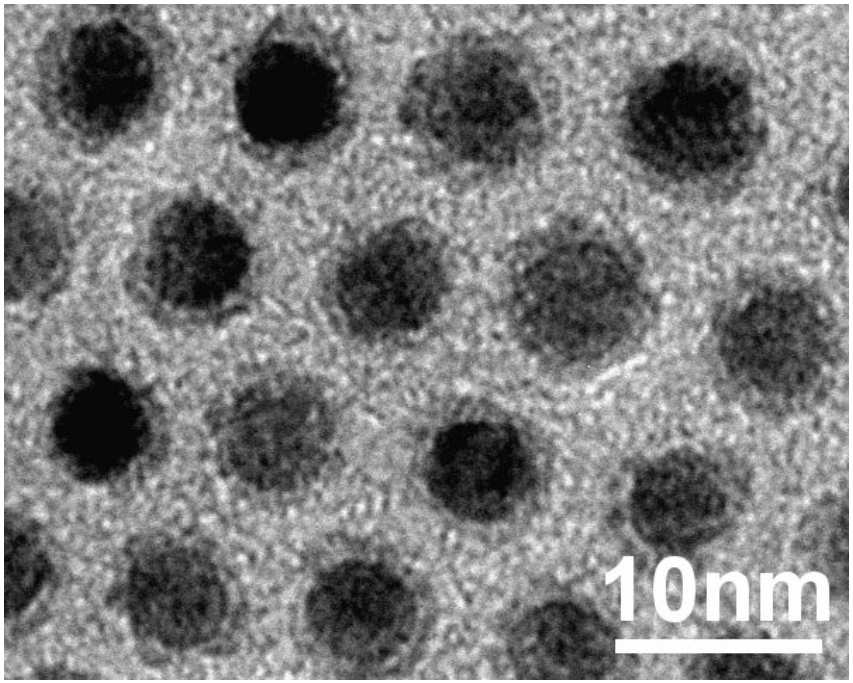
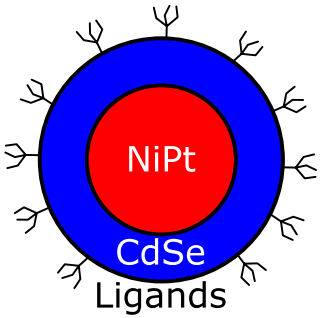
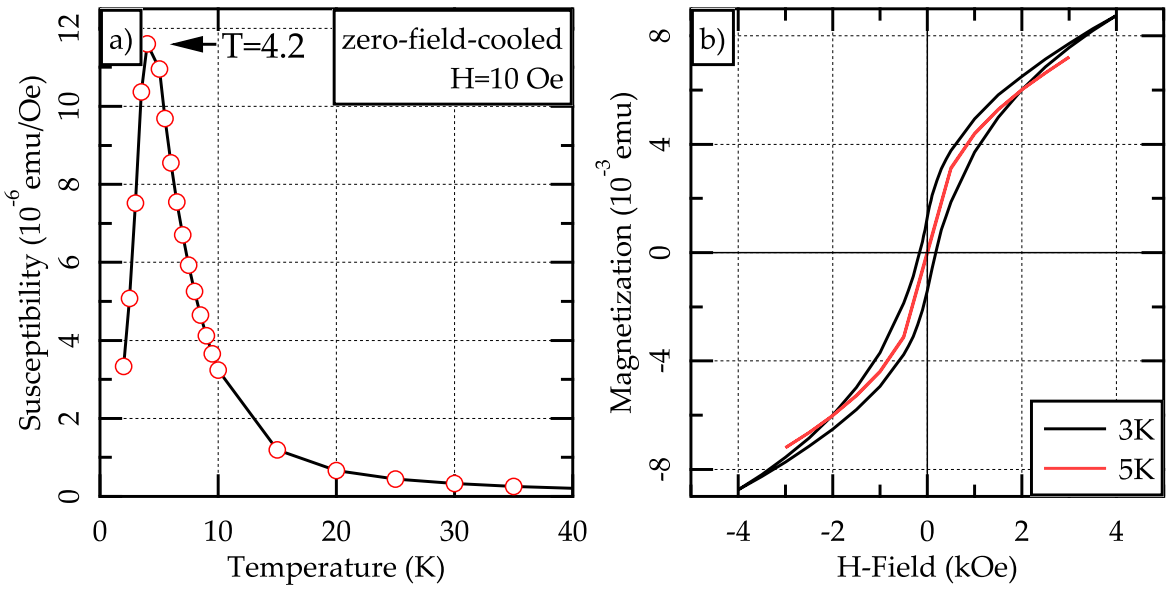
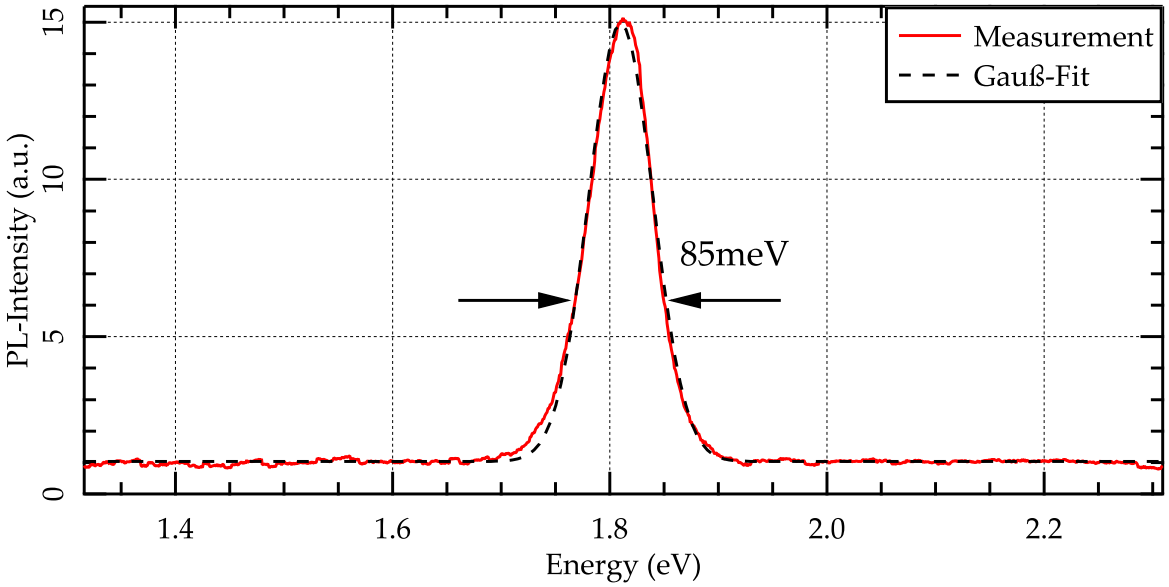


- NiPt-NCs show bocked superparamagnetism
- CdSe-NCs are well known for strong PL-signal

⇒ magnetic NiPt-core surrounded by CdSe shell

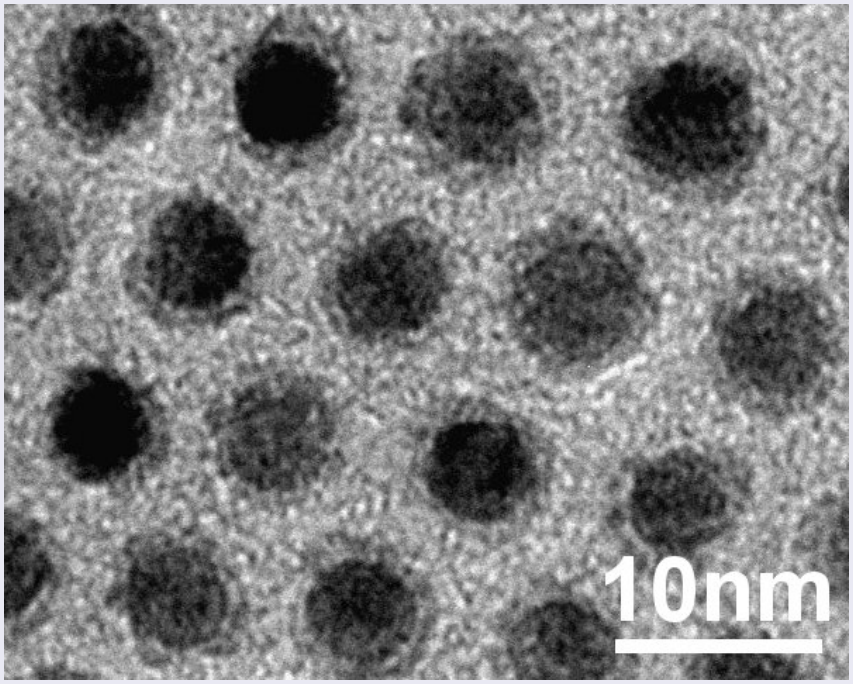



a)
T=4.2
zero-field-cooled
H=10 Oe
Susceptibility (10^{-6} emu/Oe)
Temperature (K)
b)
Magnetization (10^{-3} emu)
H-Field (kOe)
3K
5K

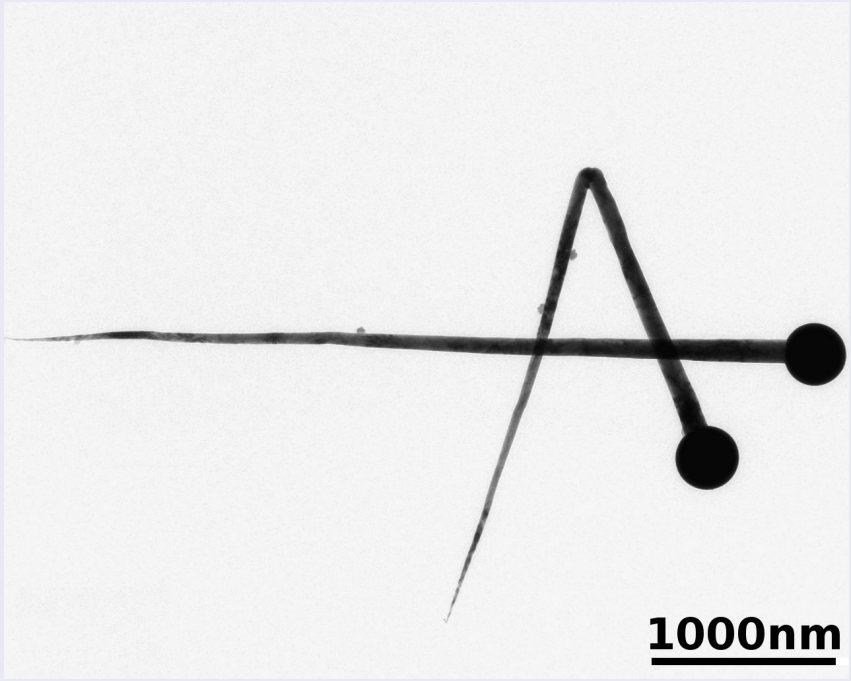

Measurement
Gauß-Fit
85meV
PL-Intensity (a.u.)
Energy (eV)

Contents

Nanocrystals

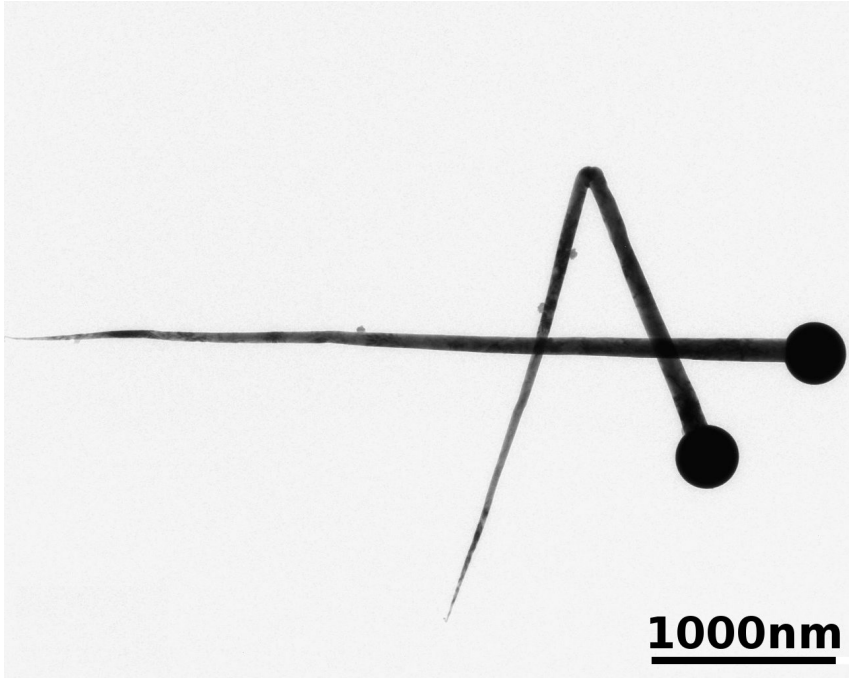


Nanoneedles



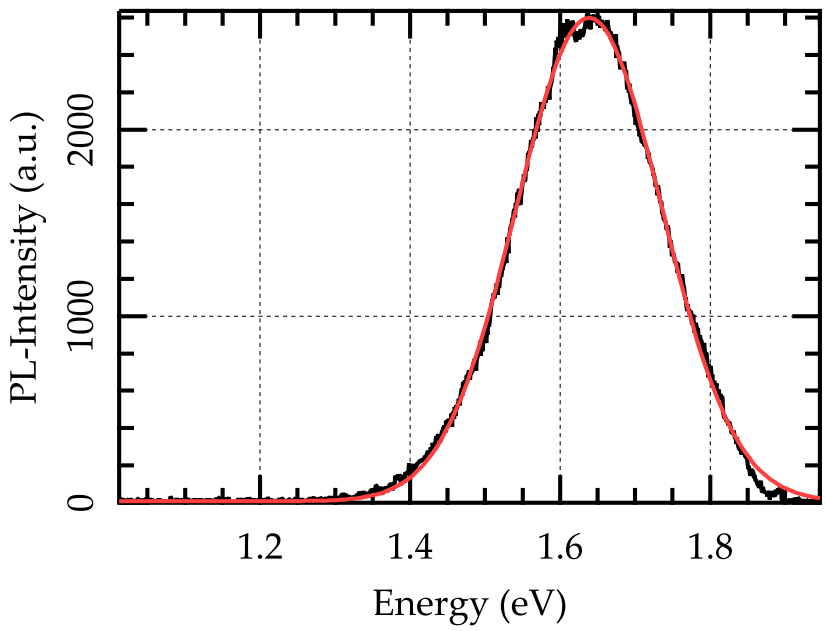
Images by Weller-Group, HH

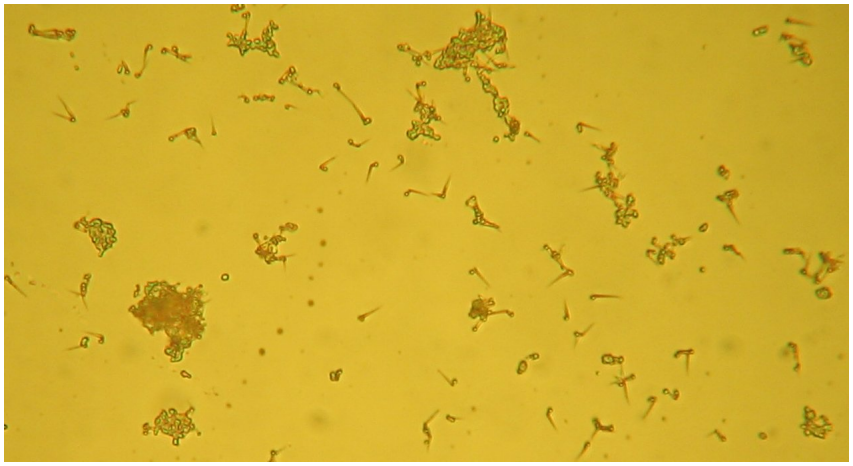
Structure



- indium-sphere ($d \approx 500$ nm)
- indiumphosphide-nanowire ($L \approx 4000$ nm)
- one-pot synthesis
- InP: direct bandgap of 1.344 eV at 295 K $\Rightarrow$ PL-signal?

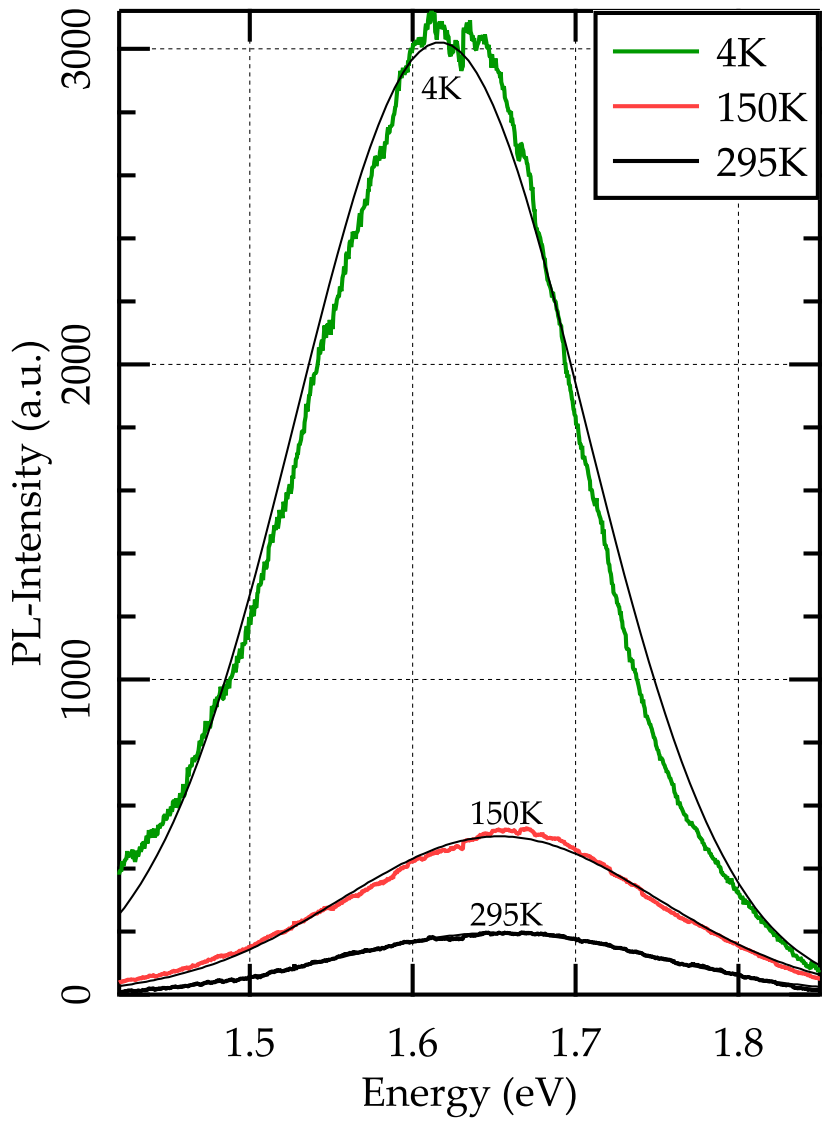
Ensemble-PL





- no PL-signal at InP-bandgap (1.344 eV) but at higher energies

Ensemble-PL

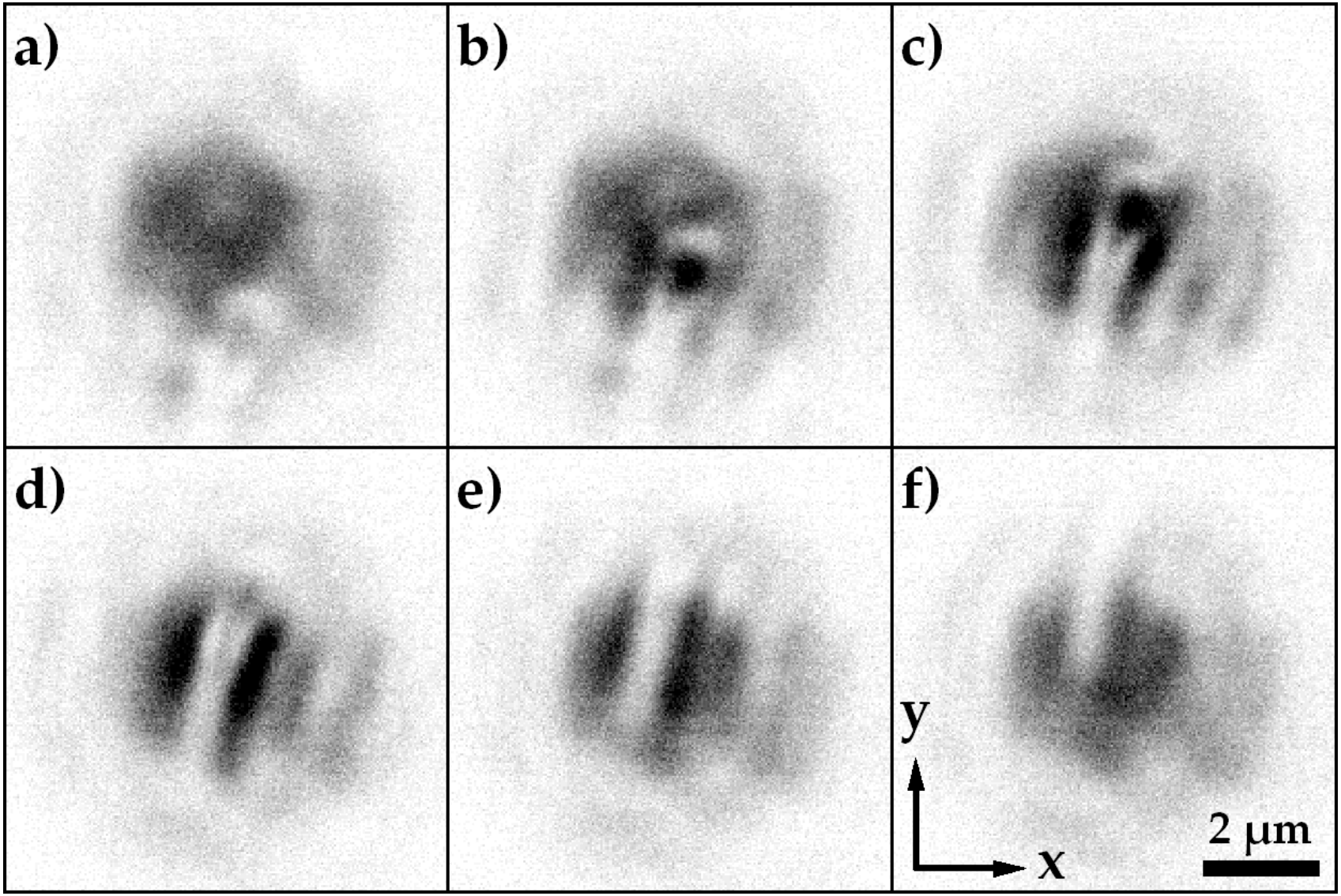


- no PL-signal at InP-bandgap (1.344 eV) but at higher energies
- strong increase of PL-intensity at low temp.
- PL-energy shifts between 4 and 150 K to lower energies (redshift)
- no shift between 150 and 295 K

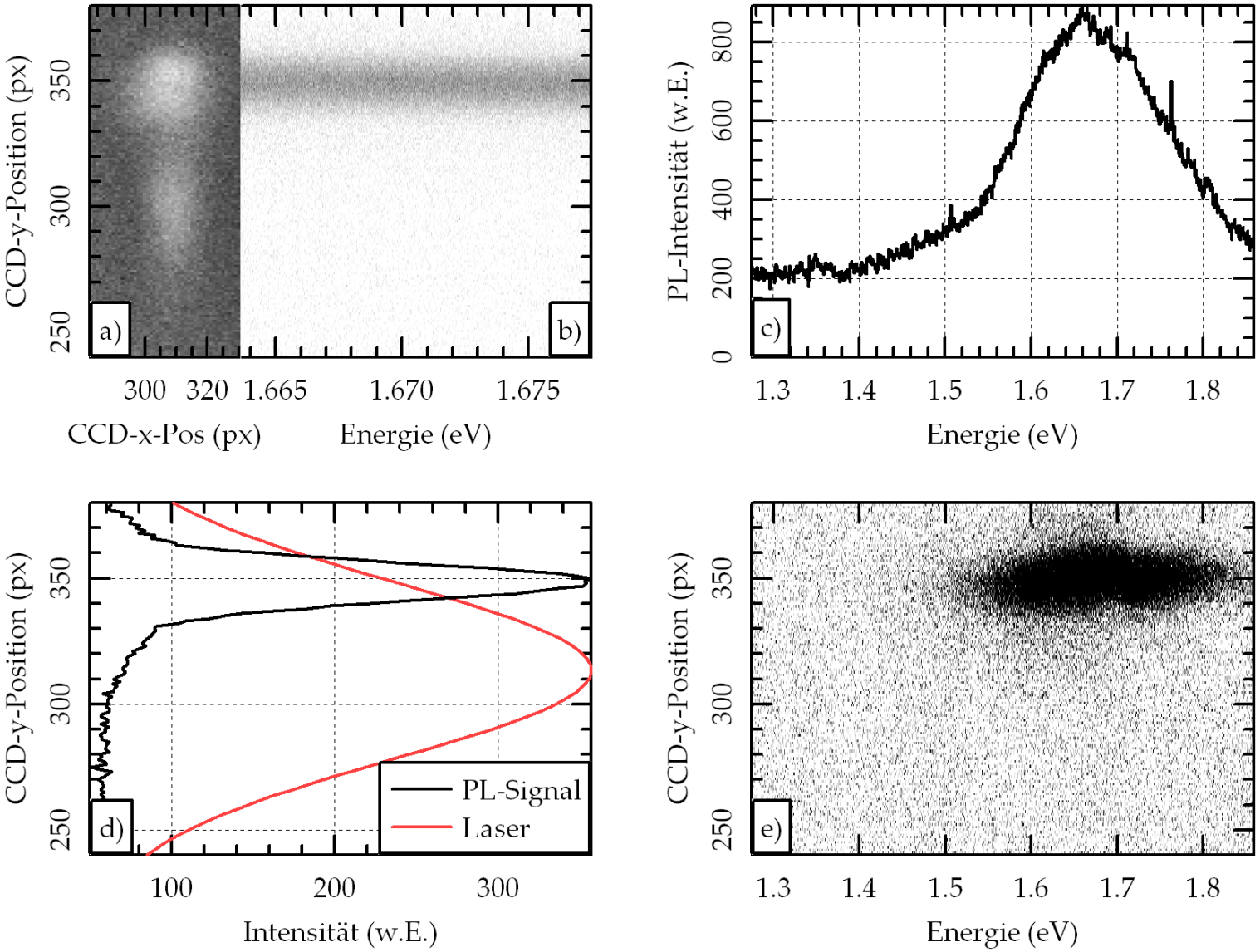
Single Needle in non-Spectral Mode

- spectrometer set to non-spectral mode (direct reflection)
- filter in front of spectrometer removes laser light
- laserspot widened to a diameter of $\approx 6\ \mu m$
- x and y coordinates of CCD-image correspond to x and y of sample
- a single needle is moved in y direction

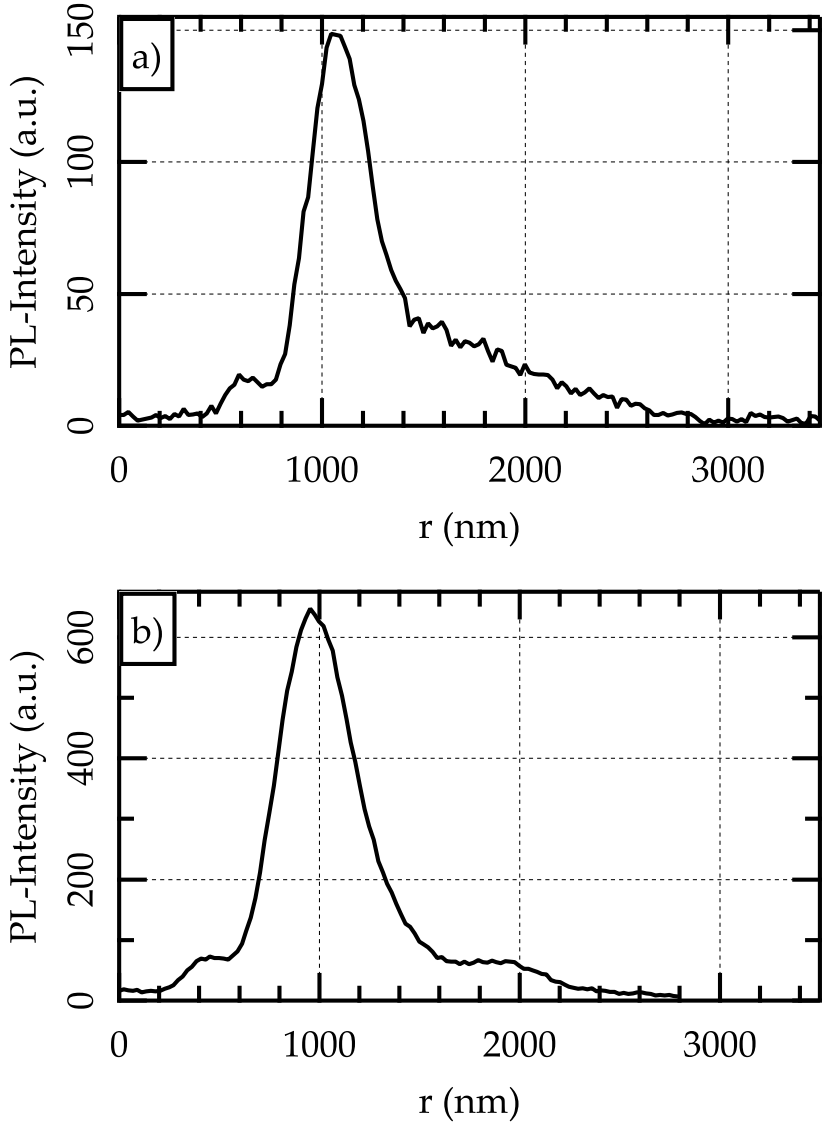
Single Needle in non-Spectral Mode



Spectral vs. non-Spectral Mode

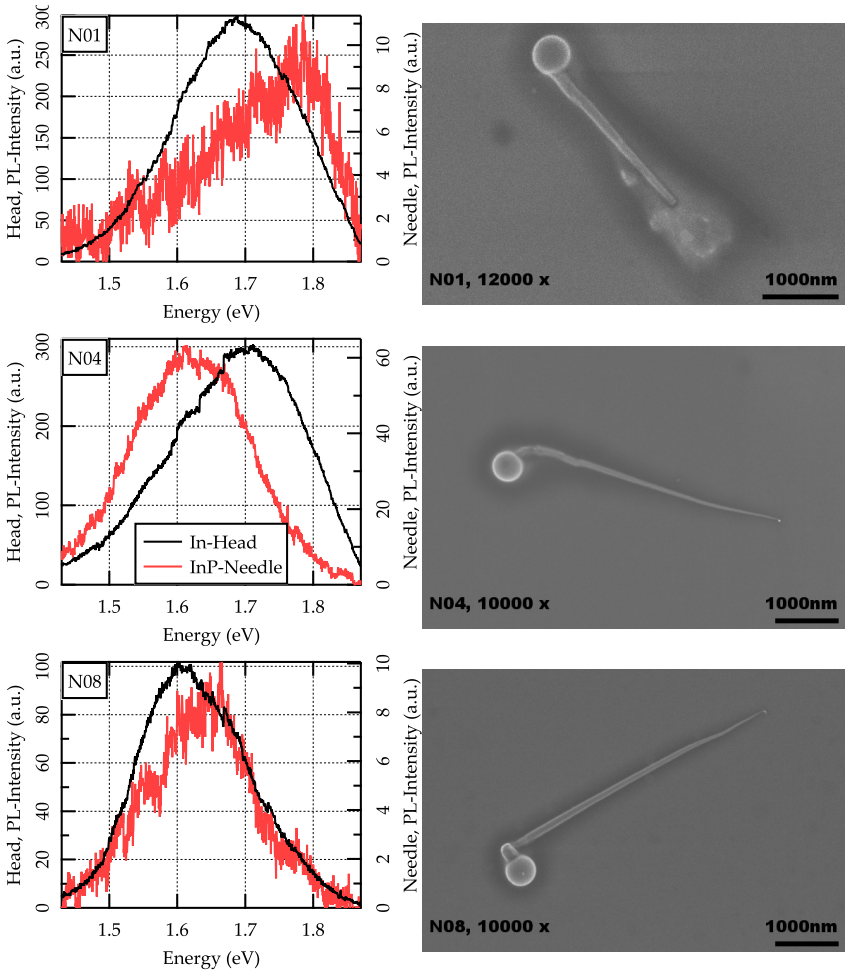


High Laser Intensity



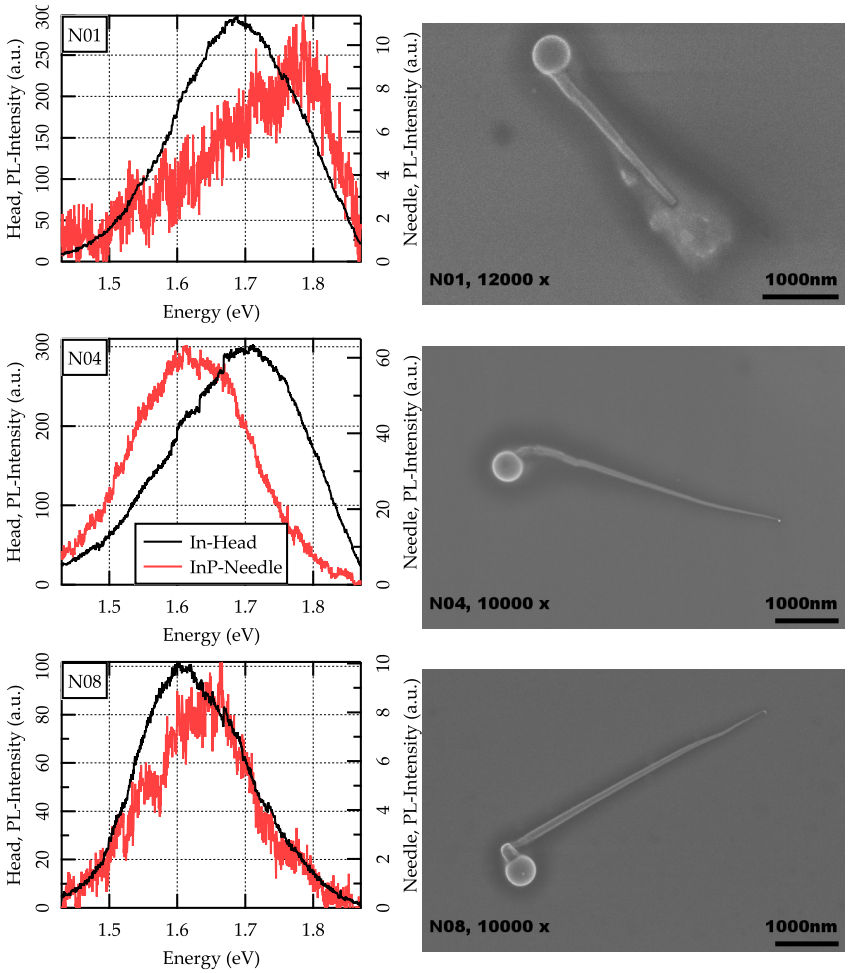
- non-spectral mode
  → spatial resolution
- PL from In-head and InP-wire

Single Needles: PL and SEM



- intensity from In-head 5-30 × higher
- no correlation between geometry and PL-signal

Single Needles: PL and SEM

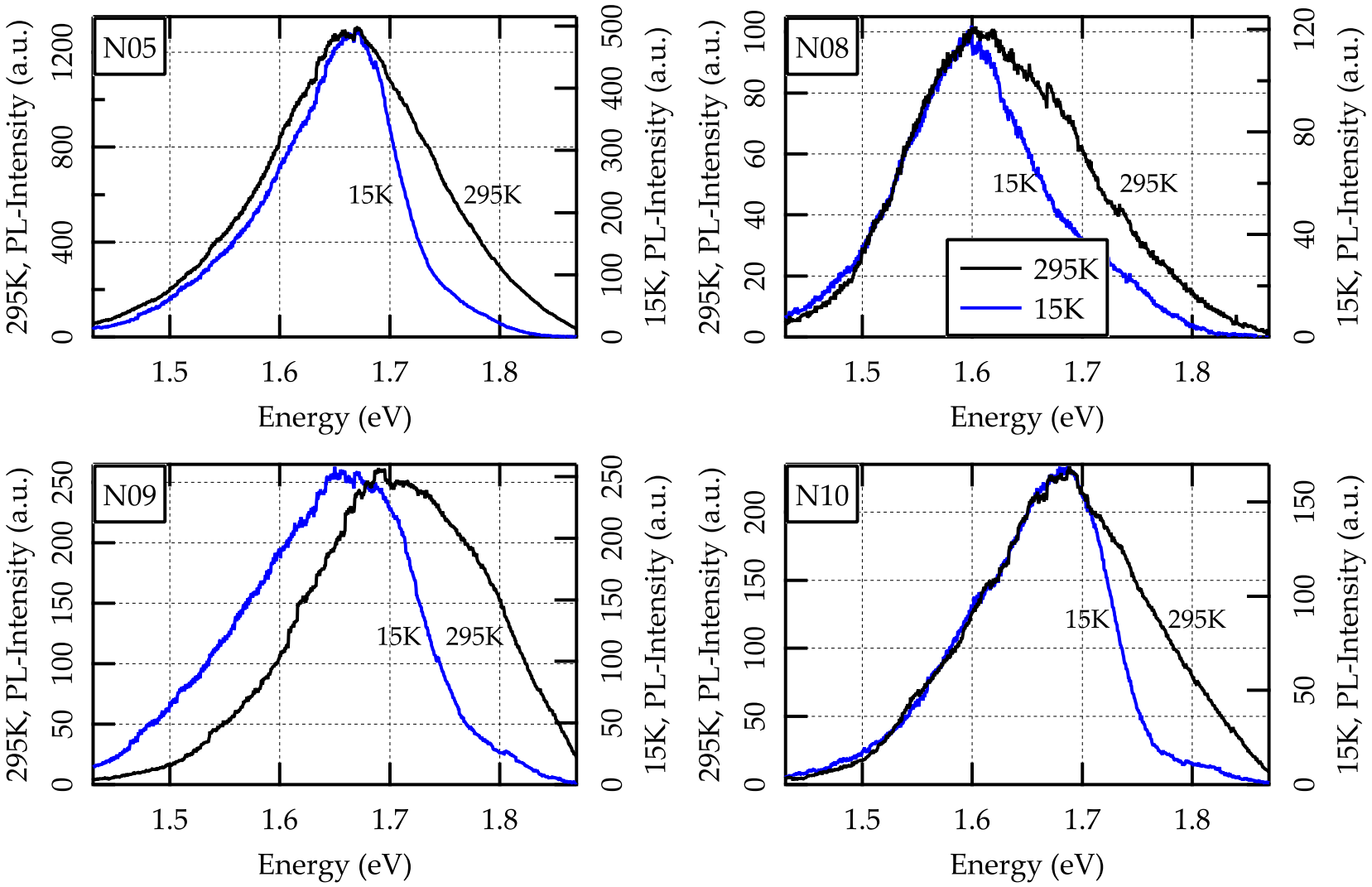


- intensity from In-head 5-30 × higher
- no correlation between geometry and PL-signal

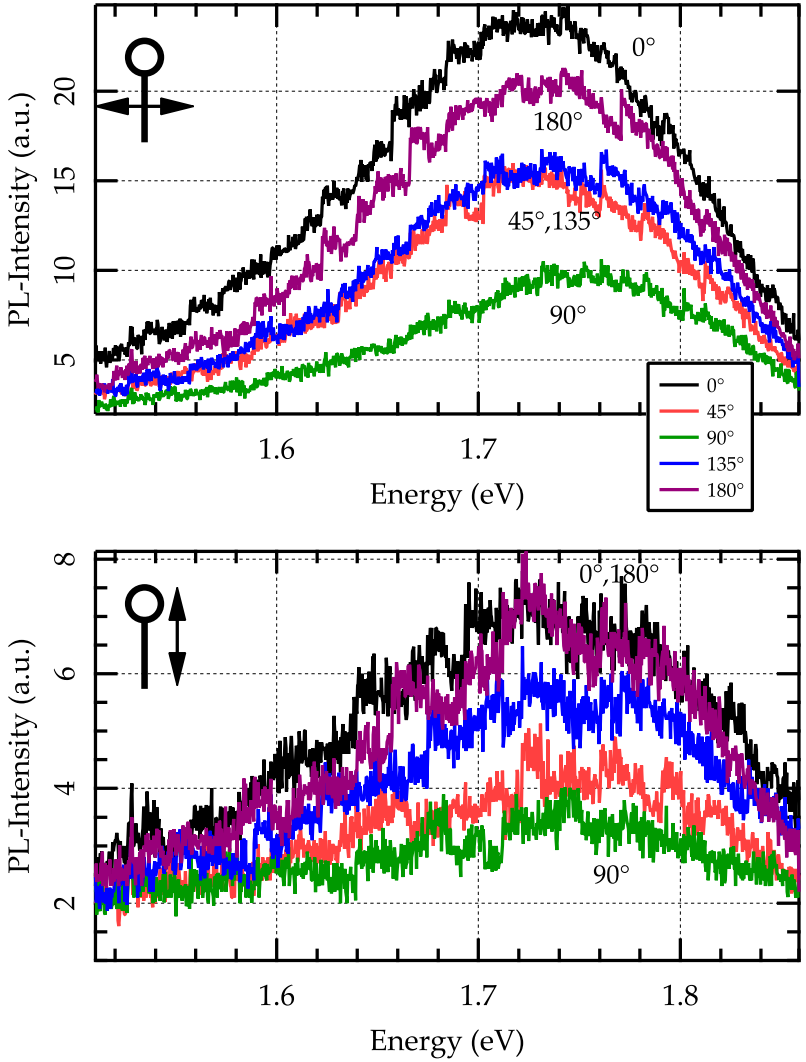
Possible Explanations

- no InP-bulk signal due to trap-states at the surface
- small InP-nanocrystals surrounding the particle might generate the PL-signal
- enhancement of NCs' PL by the In (metal) spheres

15 K vs. 295 K


N05
N08
N09
N10
15K
295K
295K
15K
295K, PL-Intensity (a.u.)
15K, PL-Intensity (a.u.)
Energy (eV)
1.5
1.6
1.7
1.8

Polarization



- PL-signal polarized in direction of needle
- polarization independent of laser's polarization
- shift the maximum can be found
- other needles show same behavior

Summary - Nanoneedles

Observations

- PL-signal $\approx$ 300 meV above InP bulk bandgap
- strong temperature dependence
- signal origins mainly from In-spheres
- no obvious correlation between geometry and PL-energy

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Summary - Nanocrystals

CdSe-NCs

- moved experiment to a new lab
- successfully investigated ensembles and single NCs
- temperature dependency of ensemble-PL
- pumping of NCs by others
- shifting and blinking of single NCs
- low signal-to-noise ratio

Acknowledgment

Prof. Dr. Detlef Heitmann
Prof. Dr. Horst Weller
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