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School of Physics and Astronomy

Quantum effects in colloidal nanoparticles

From the beauty of single quantum dot physics

to ensemble applications ...

Prof Pavlos Lagoudakis

Ioffe 10/06/2013

Colloidal nanocrystals: nano-engineering

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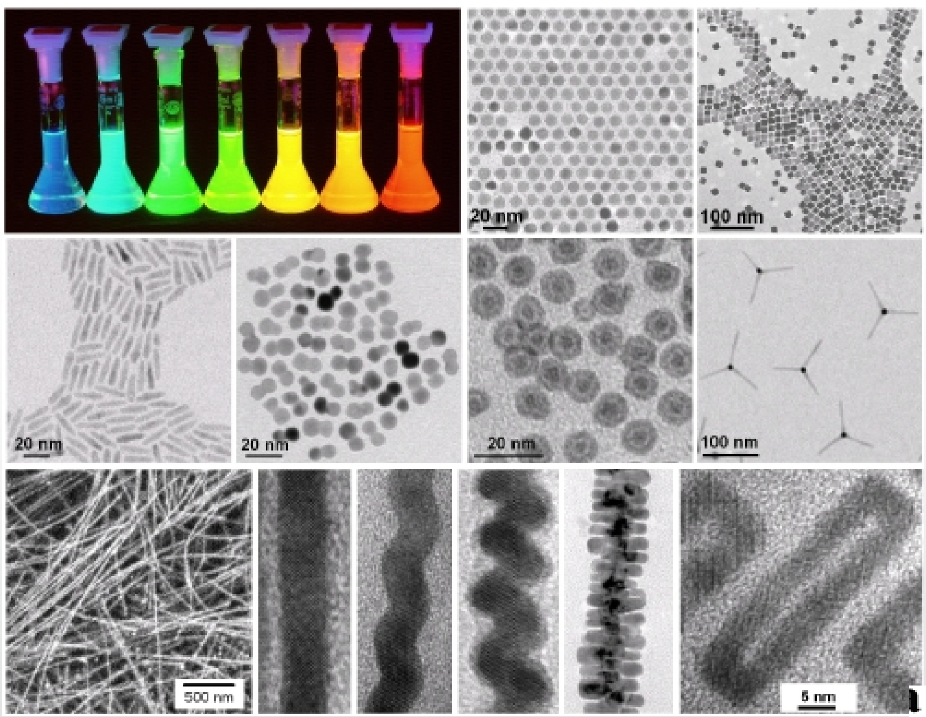
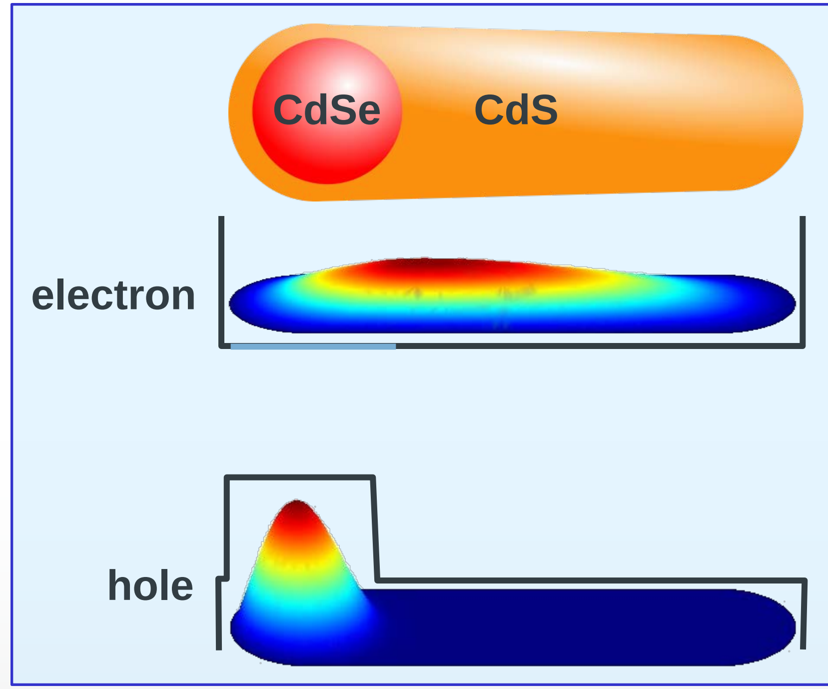
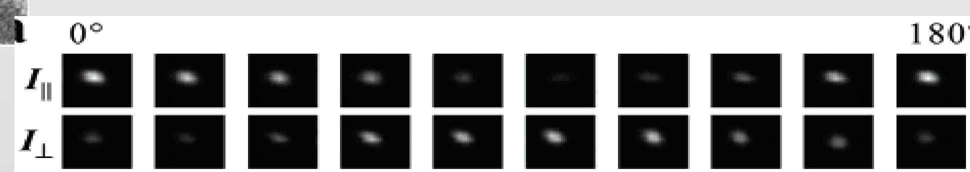
- low cost chemical synthesis
- optical tunability through size
- shape versatility



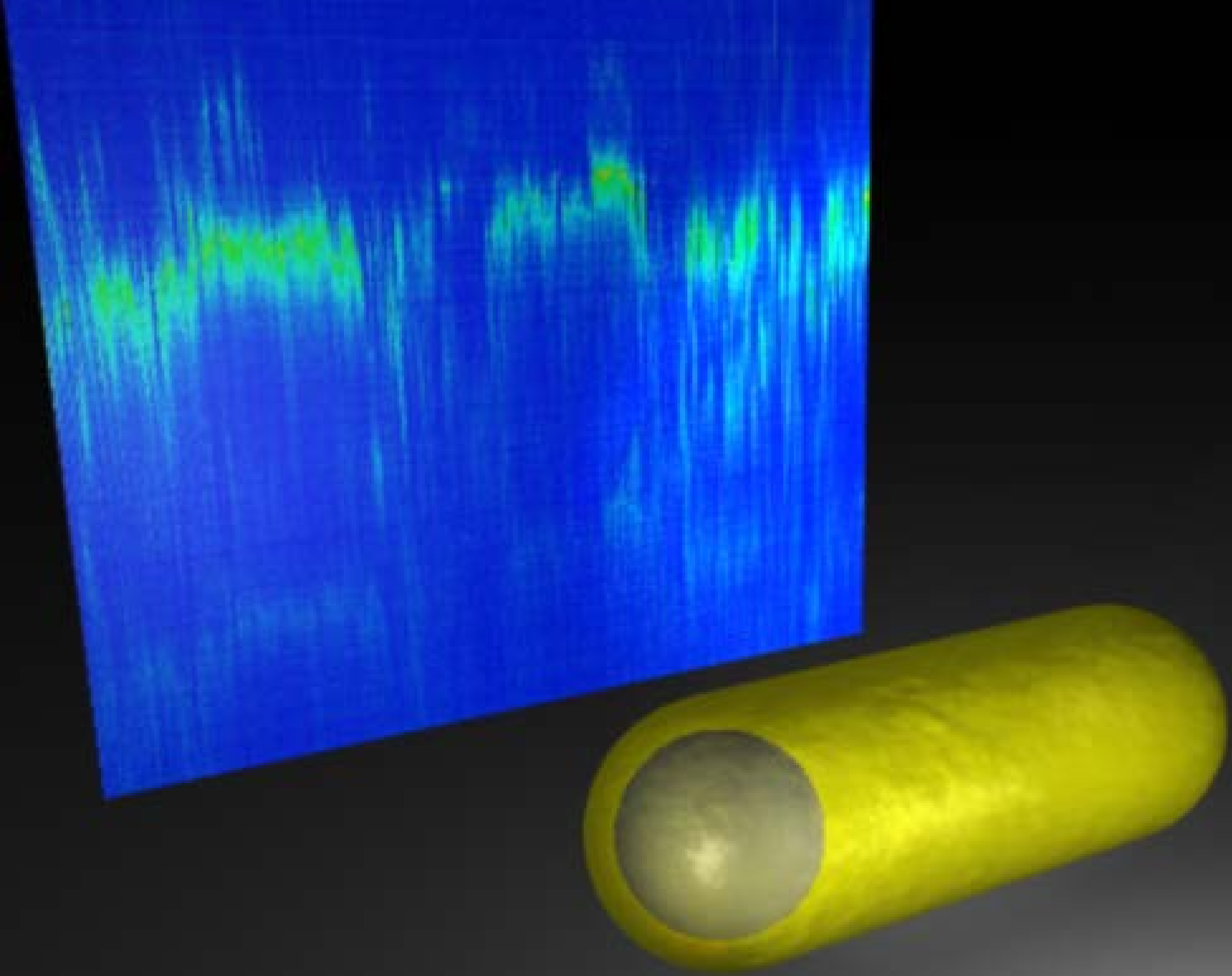
http://chemistry.uchicago.edu/fac/talapin.shtml



- hole confined to core, electron spreads over whole length ~16nm
- nanorods of **mixed dimensionality**
- highly polarised luminescence



Talapin et al., *Nano Letters*, **3**, 1677



Single Particle Spectroscopy

Single Particle Spectroscopy

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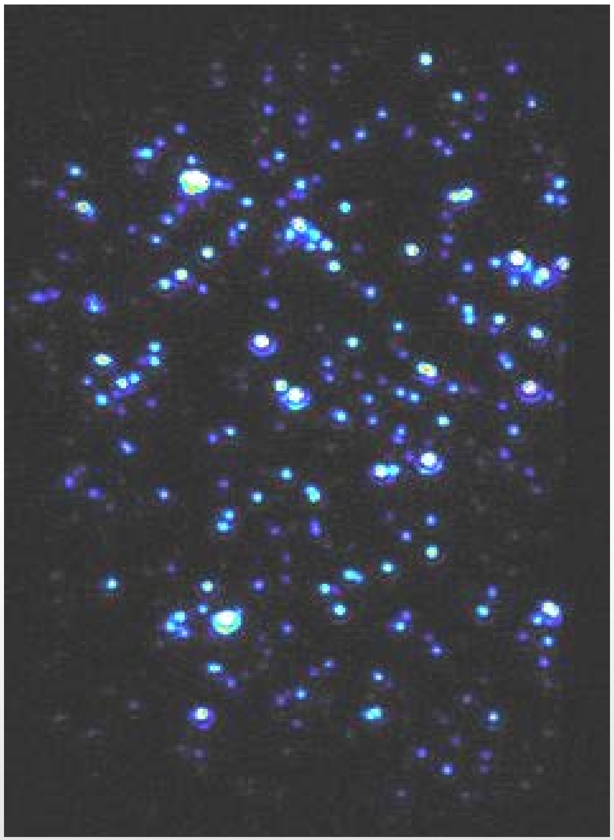
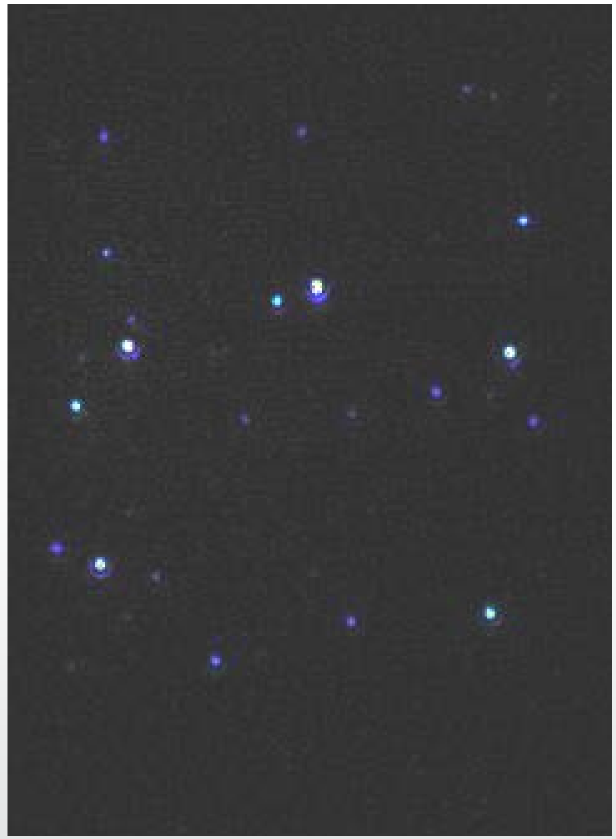
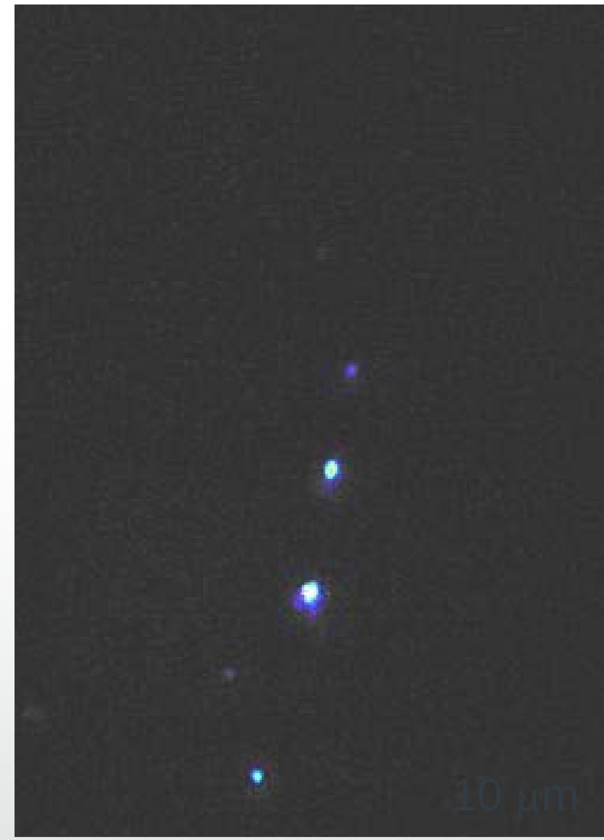
10^{-5} mg/ml



10^{-6} mg/ml



10^{-7} mg/ml



Changing particle concentration

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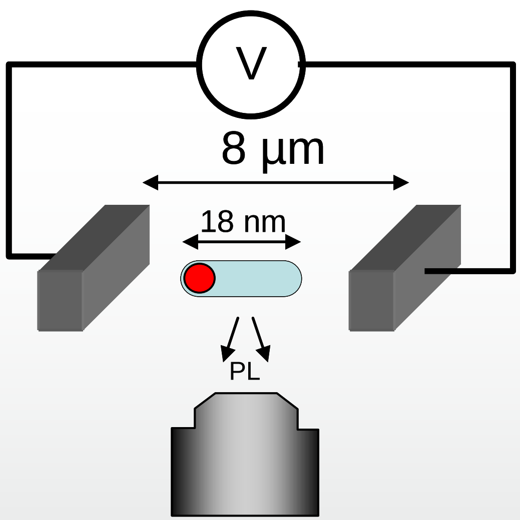
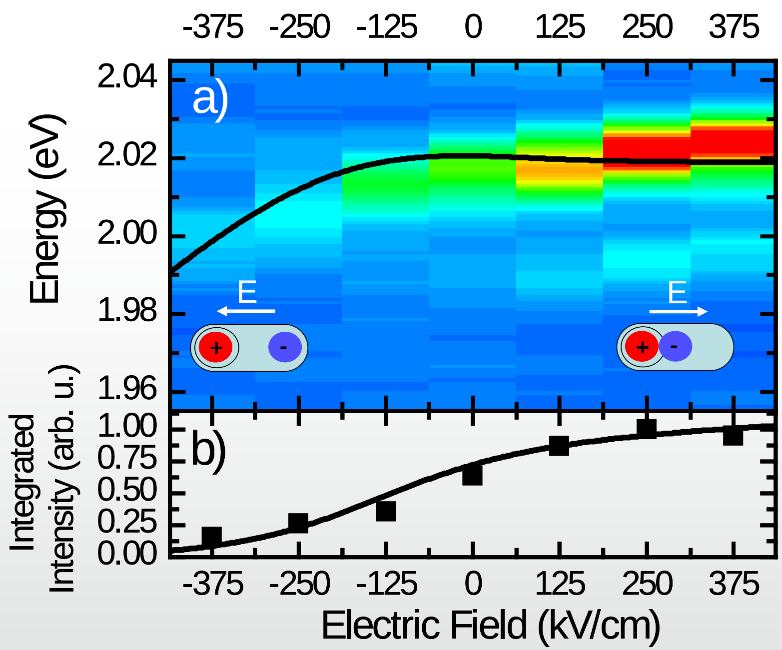
Manipulate brightness with external electric field





- Manipulating oscillator strength

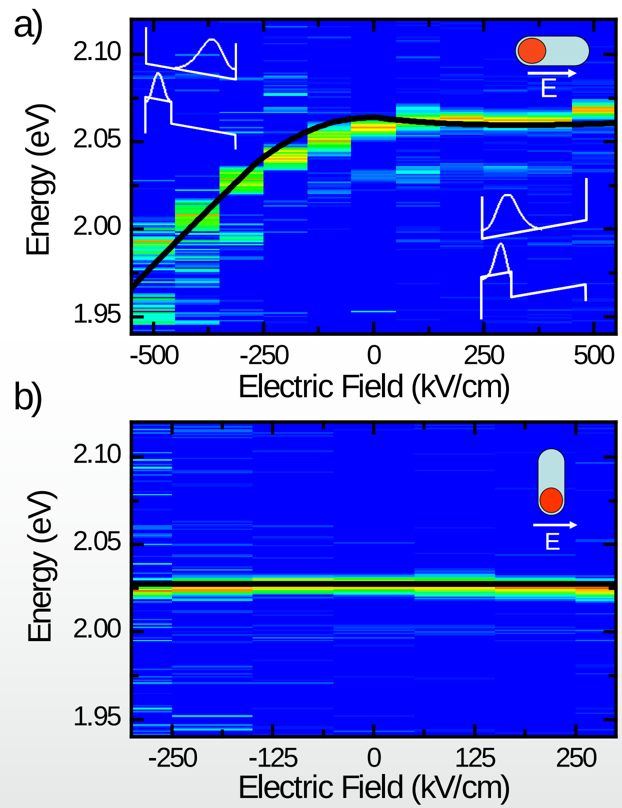
Tune photoluminescence energy

$$\left(\frac{\hbar^2\pi^2}{2m_e^*(\vec{r})}\Delta + V_{cb}(\vec{r}) + V_h(\vec{r}) + V_{ext}(\vec{r})\right)\Phi_e(\vec{r}) = E_e\Phi_e(\vec{r}) \quad (1)$$

$$\left(\frac{\hbar^2\pi^2}{2m_h^*(\vec{r})}\Delta + V_{vb}(\vec{r}) + V_e(\vec{r}) - V_{ext}(\vec{r})\right)\Phi_h(\vec{r}) = E_h\Phi_h(\vec{r}) \quad (2)$$

where V_{vb} and V_{cb} are the valence and conduction band potentials, respectively, and V_{ext} indicates an external potential due to an applied electric field, which is initially set to zero.

The wave functions are solved iteratively using a finite element method with a sequential optimization of $V_{e,h}$ following the Hartree self-consistent potential approach



- enhanced Quantum Confined Stark Shift (up to 100 meV) at 4K

Muller et al Nano Letters Vol. 5, No. 10 2044-2049
Kraus et al Phys. Rev. Lett. **98,** 017401

Experimental Setup

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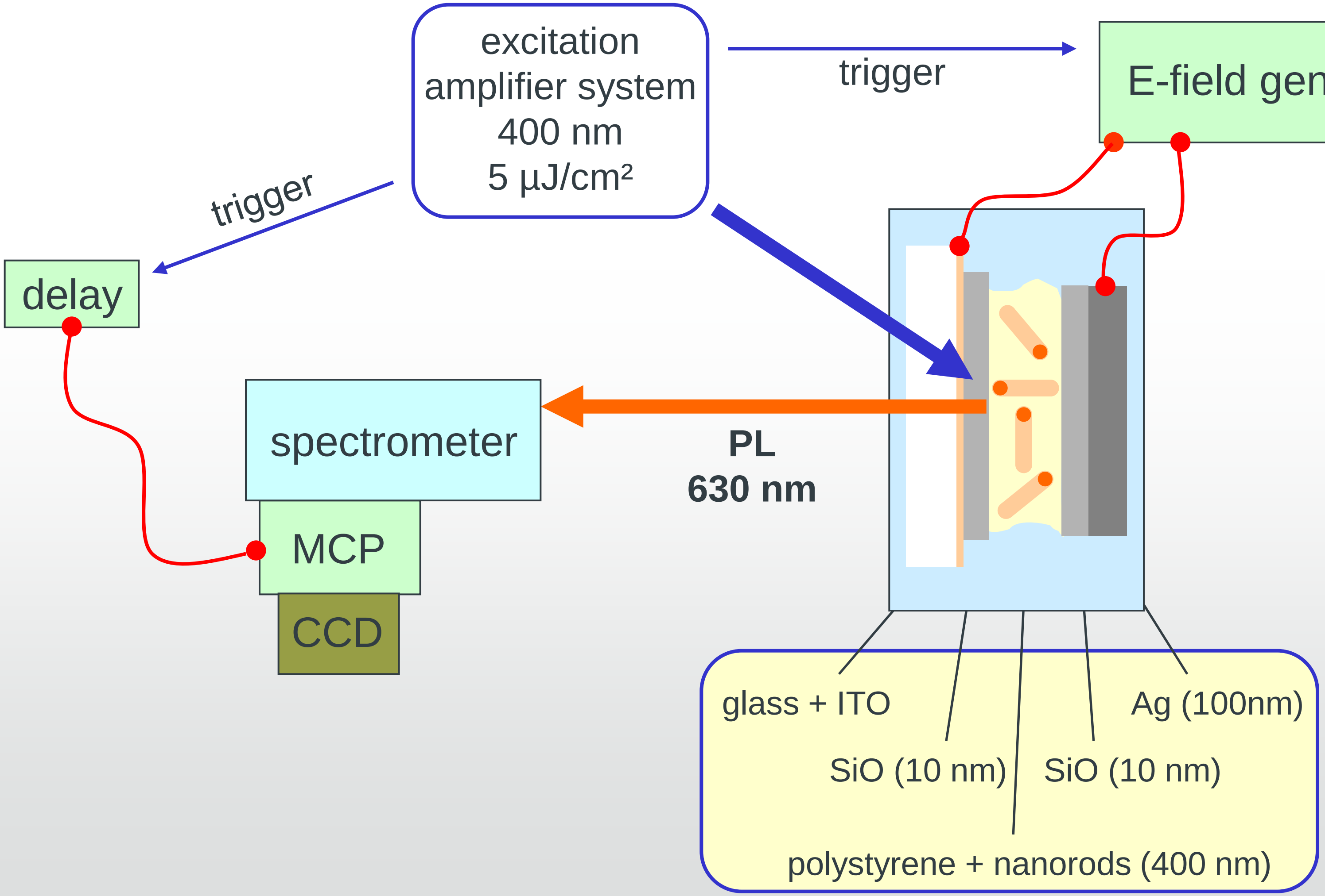
Goal: Control the emission properties with applying an electric field



Manipulating the wavefunctions in the ensemble

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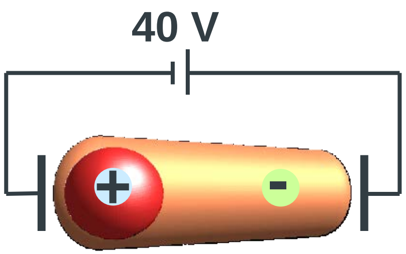
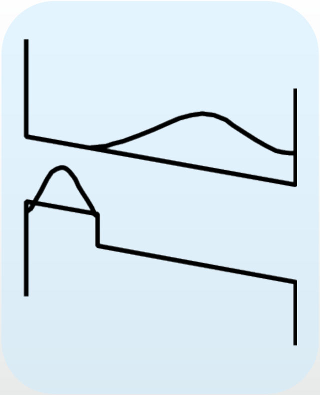
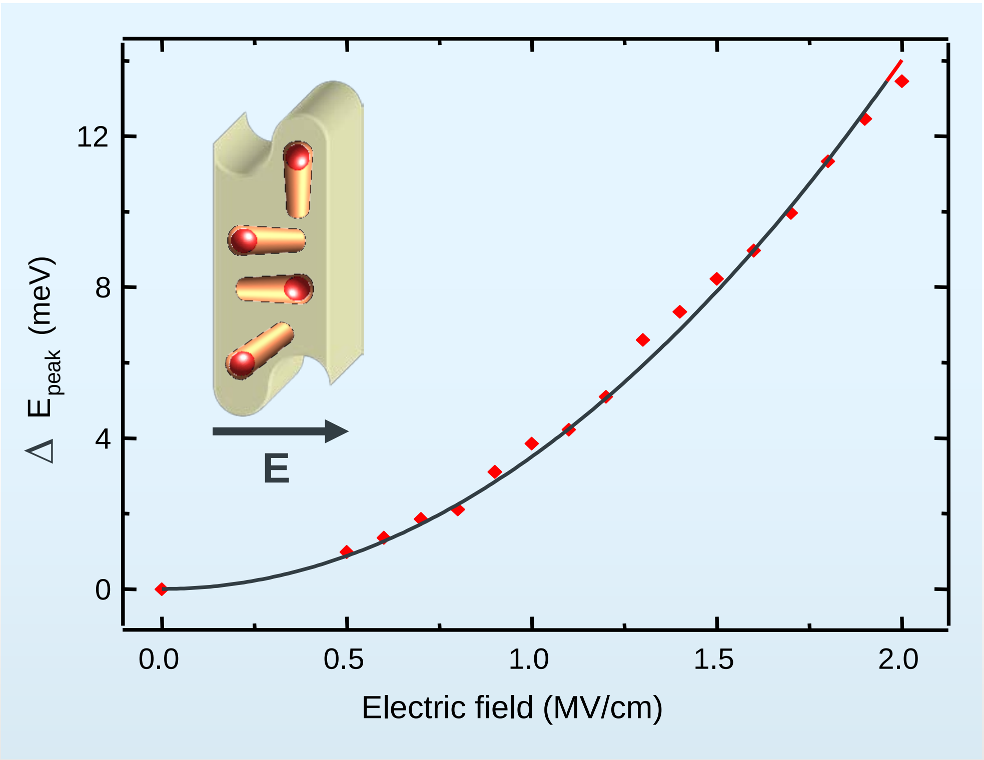
QCSE in ensemble of nanorods







Quadratic Stark effect of up to 14 meV

Gated Photoluminescene

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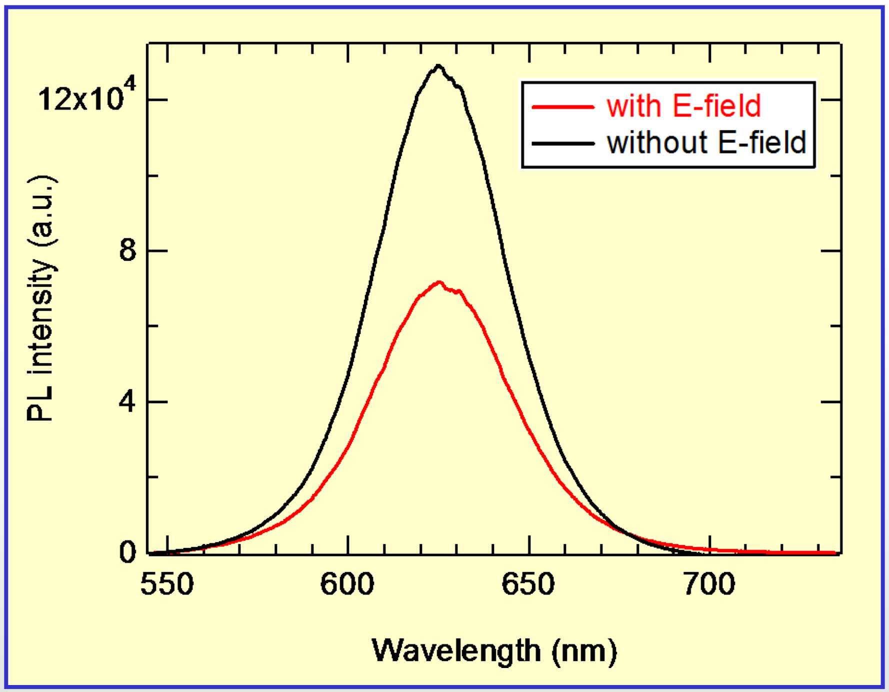

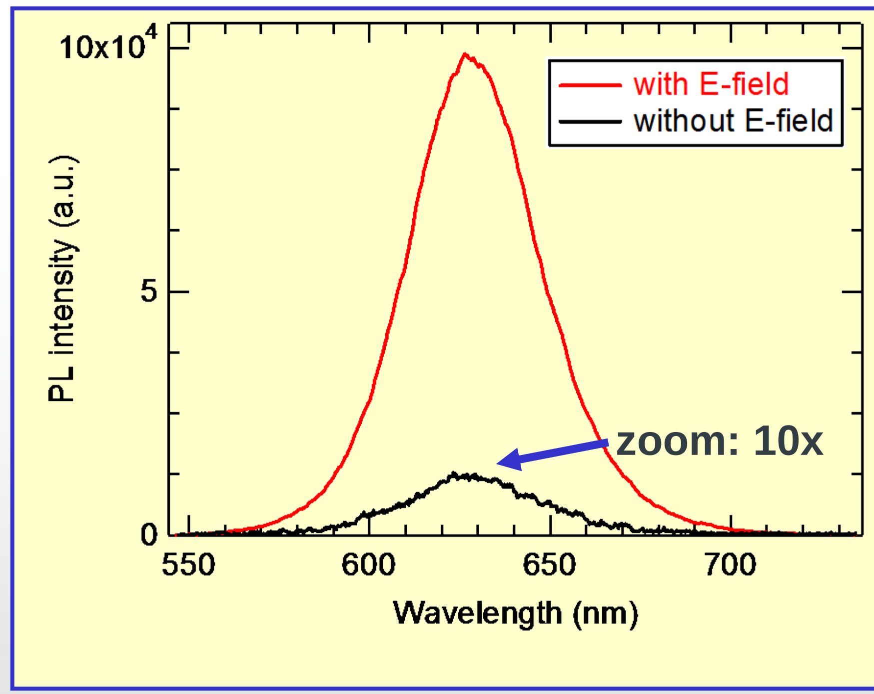

PL quenching

PL burst

Kraus et al Phys. Rev. Lett. **98,** 017401

at room temperature

Photoluminescence Quenching and Burst

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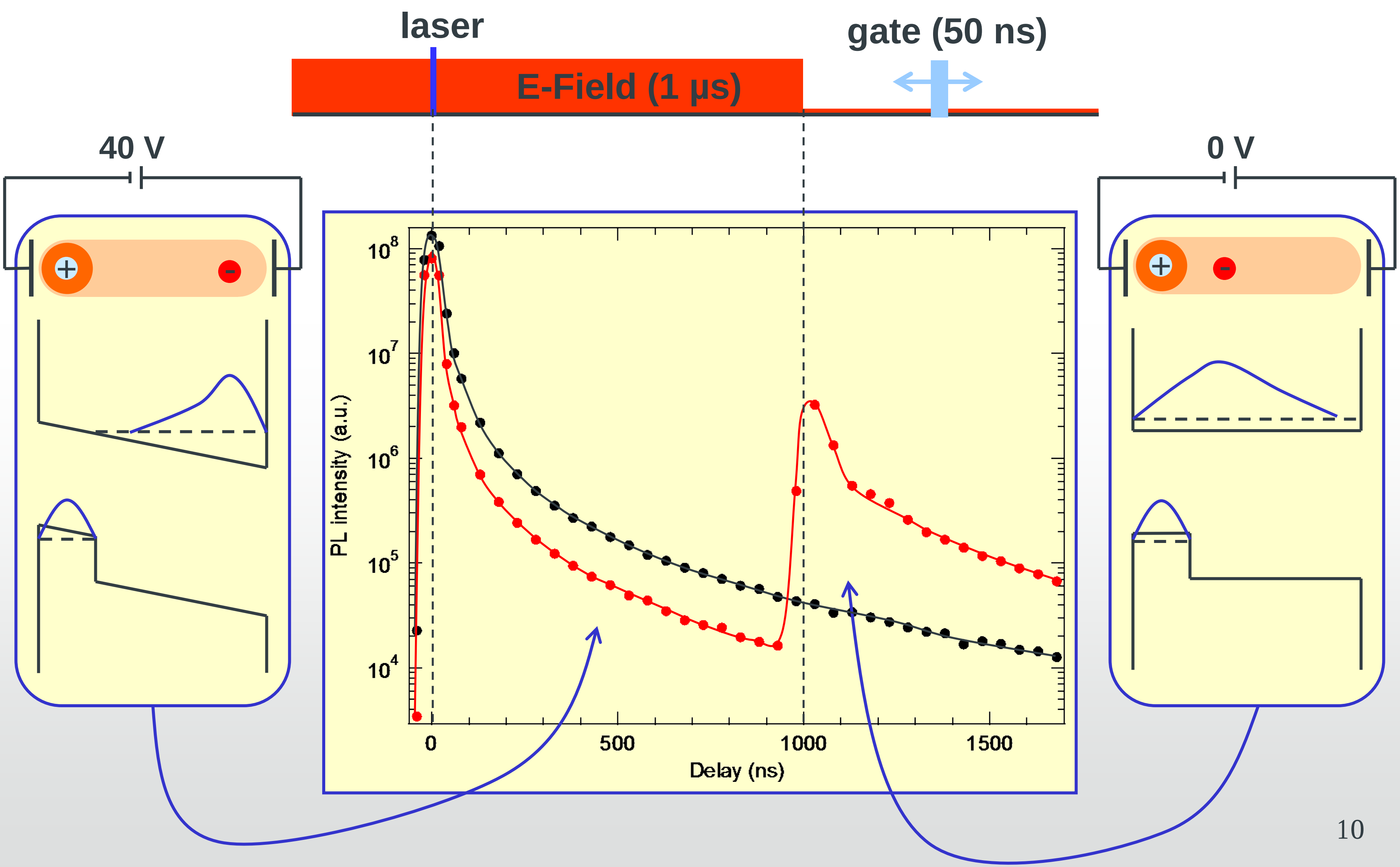
School of Physics and Astronomy



Exciton Storage

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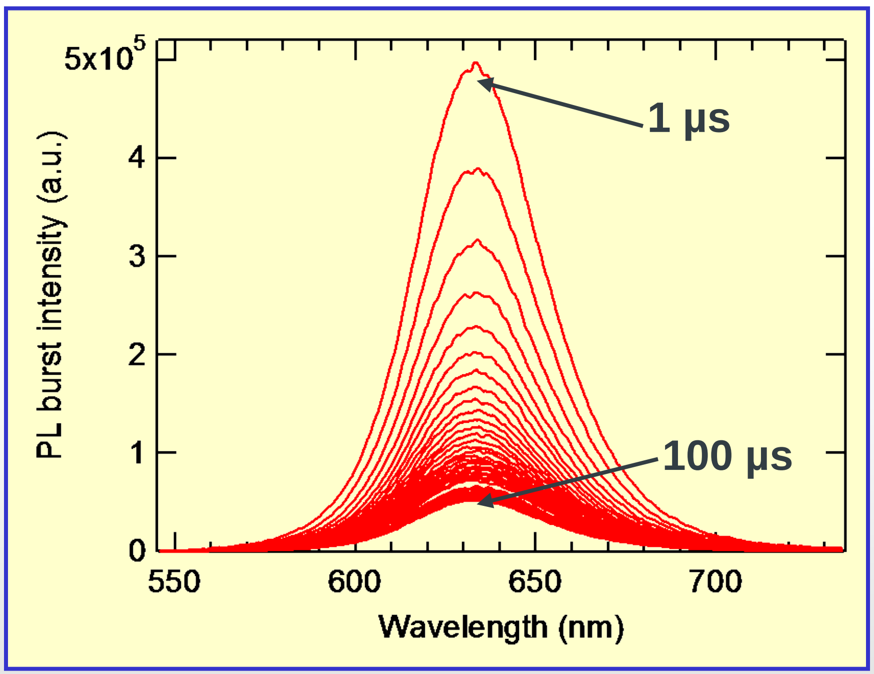
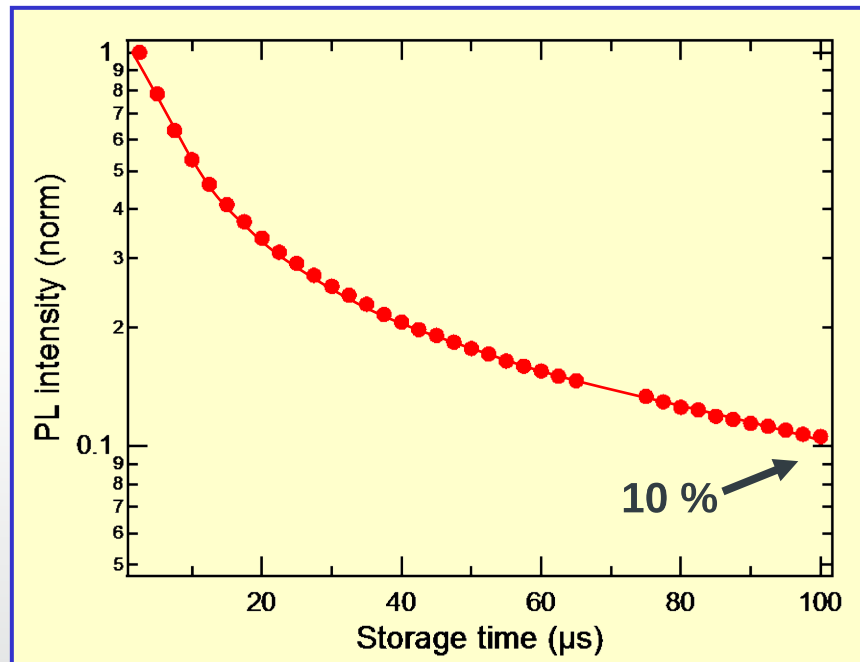
School of Physics and Astronomy





Sufficient exciton storage up to 100 µs!

Device!

Kraus et al Phys. Rev. Lett. **98,** 017401

Burst E-field Dependence

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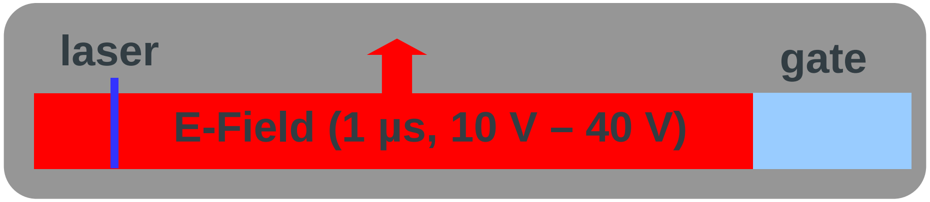

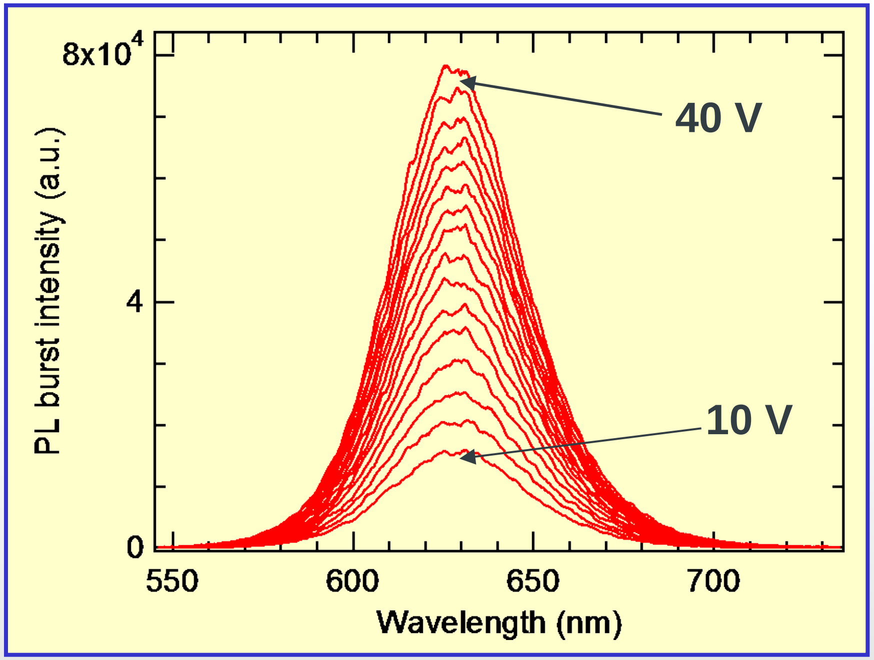

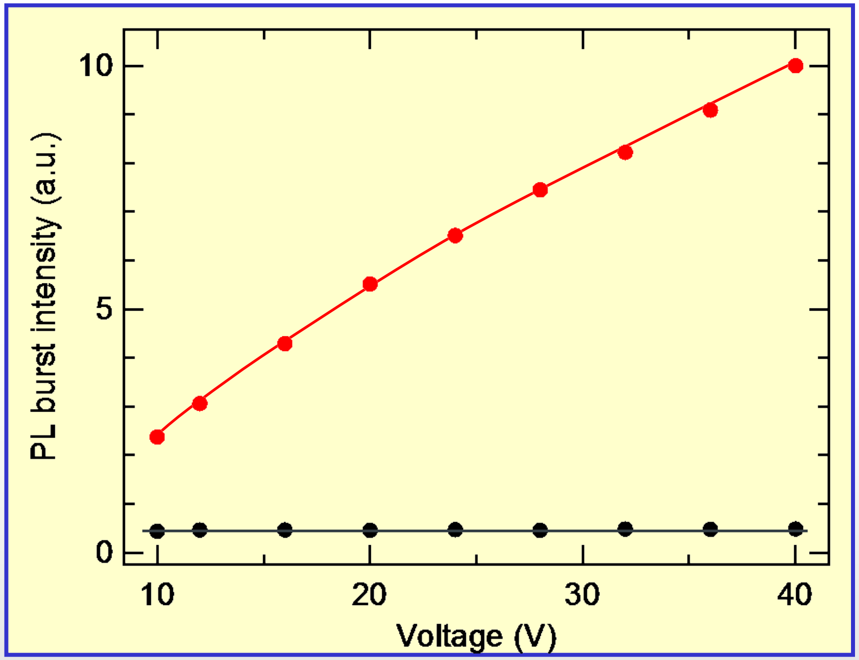

Controlling amount of exciton storage!

Kraus et al Phys. Rev. Lett. **98,** 017401

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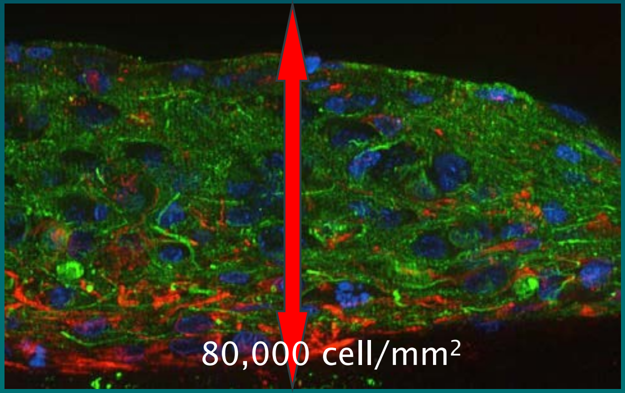
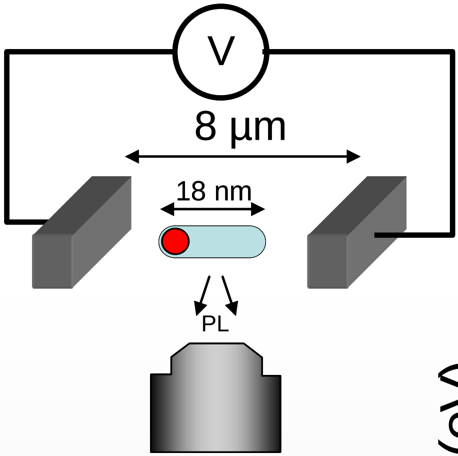
The interface to
Life Sciences

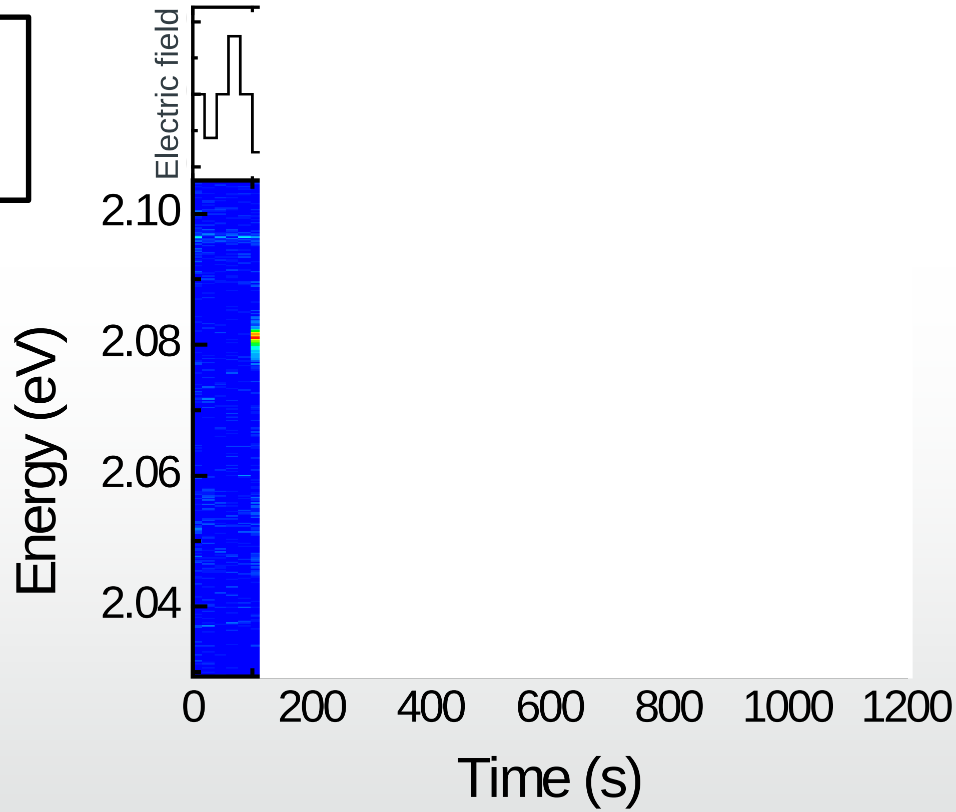
Hi-spots: used by pharmaceuticals



Brain

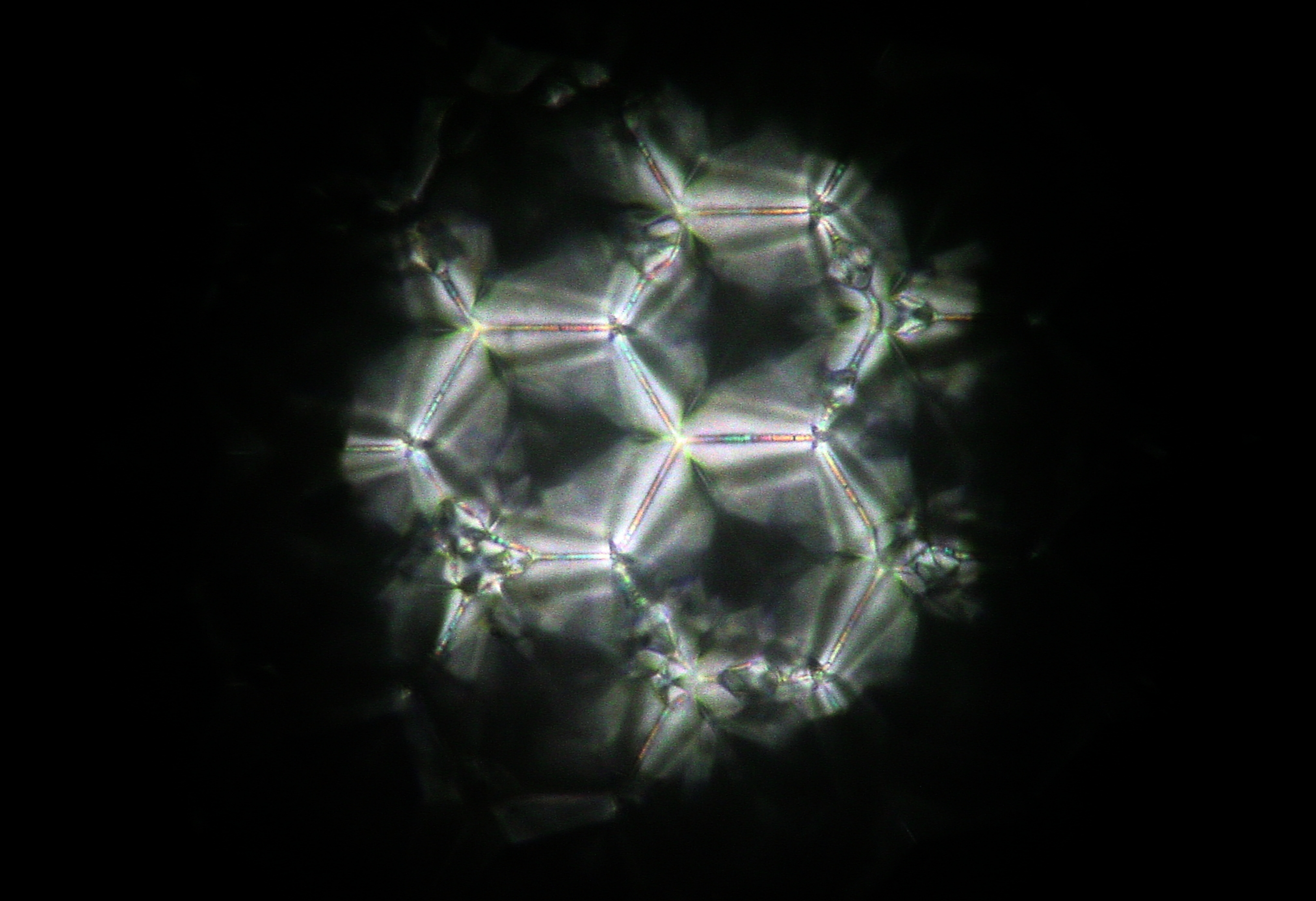
Neurophotonics



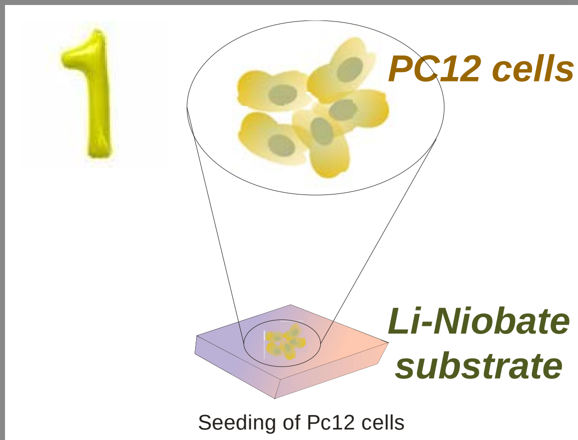


Reversely: E-field sensors at the nanoscale

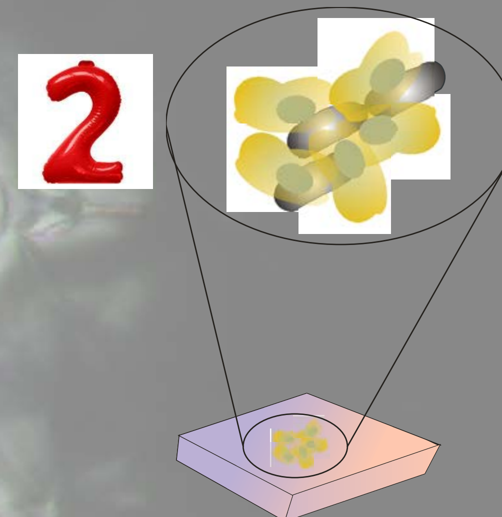
Controlling alignment of nanocrystal networks



Controlling alignment of nanocrystal networks

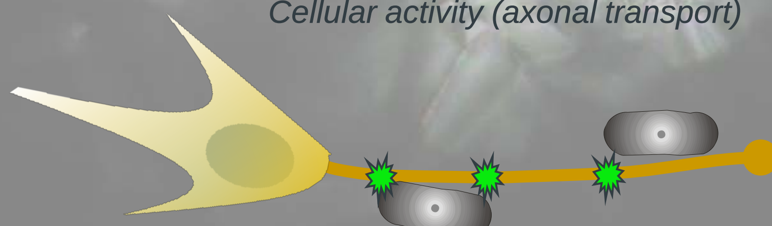


Use of nanocrystals
underneath the cell layer

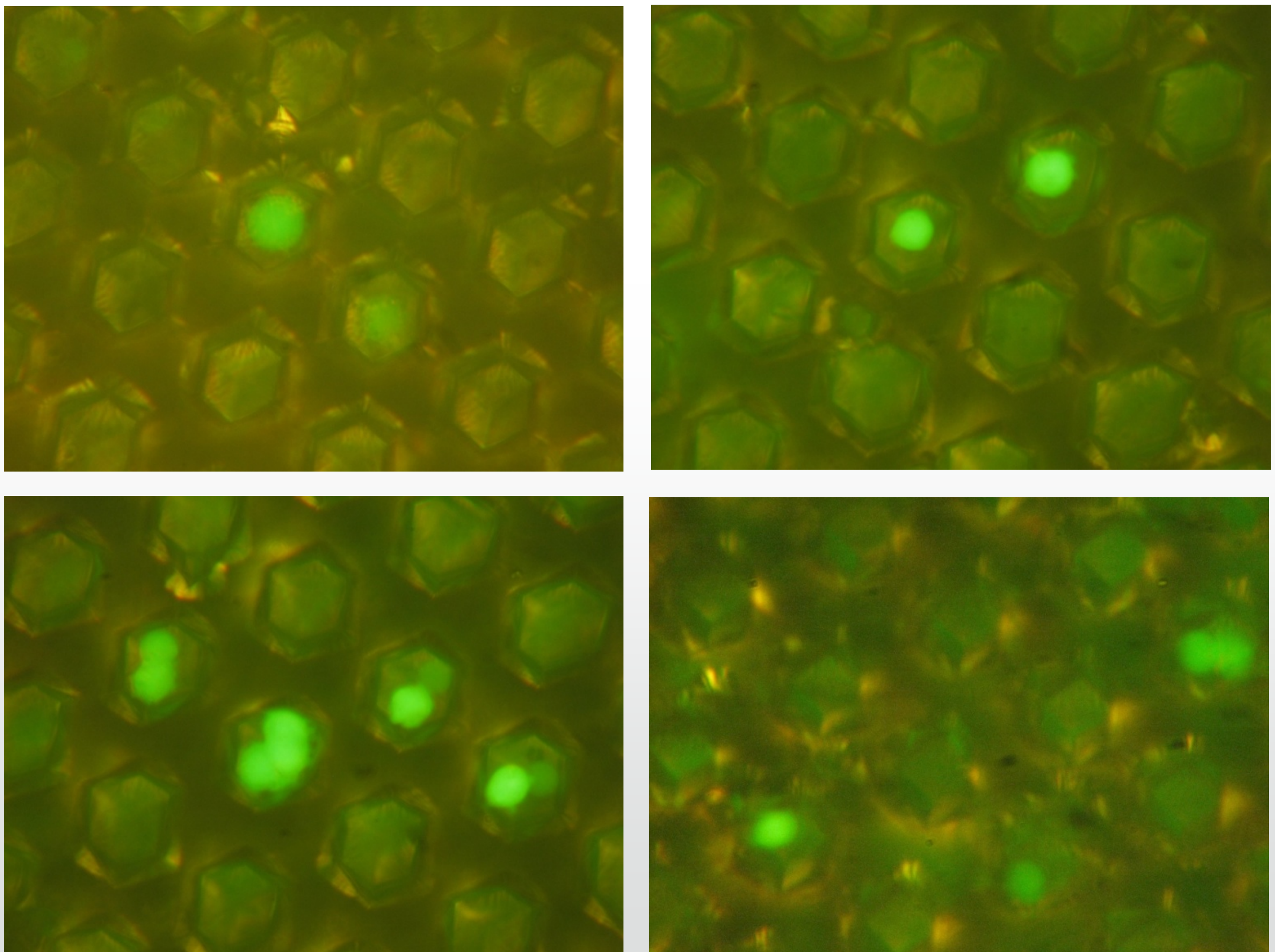


Interrogating Neuronal Activity

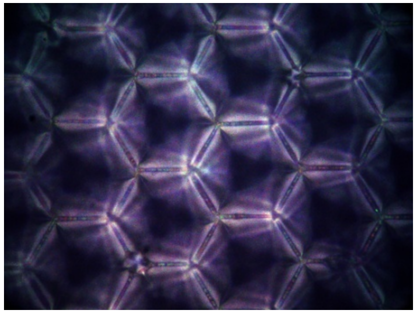
Electrical activity (action potential)
Cellular activity (axonal transport)



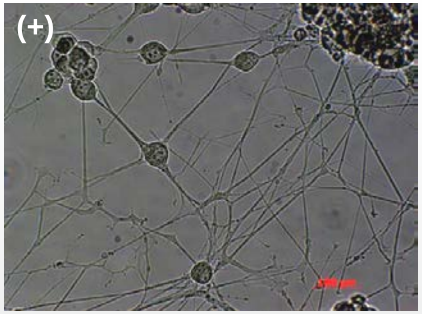
Control growth localisation of cells

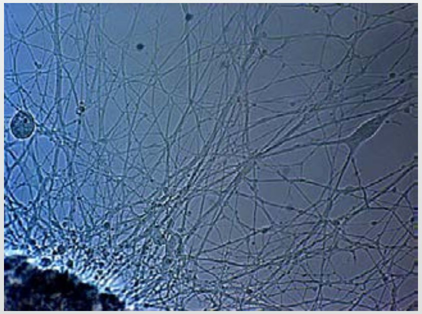


Intercepting Neural Signalling



Spatial alignment of nanocrystals





cell/neuritis-growth

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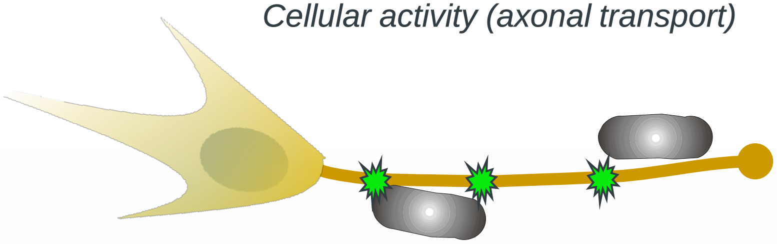
Cellular activity (axonal transport)



Phd project on Neuro/Nano-science
Postdoctoral position available

School of Physics and Astronomy
School of Biological Sciences

Prof Pavlos Lagoudakis
email: lagous@soton.ac.uk

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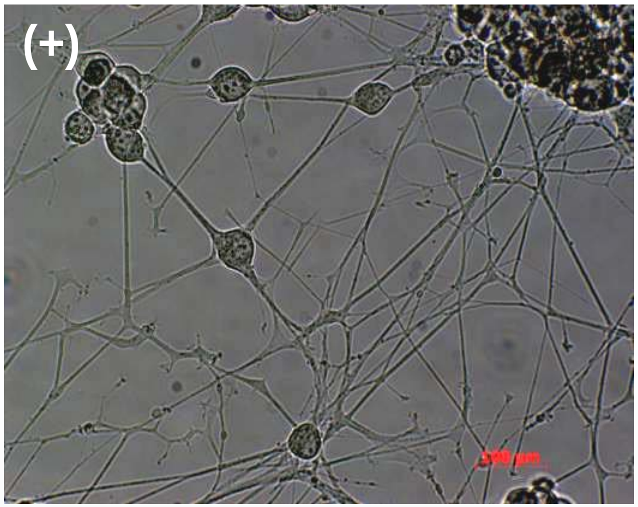
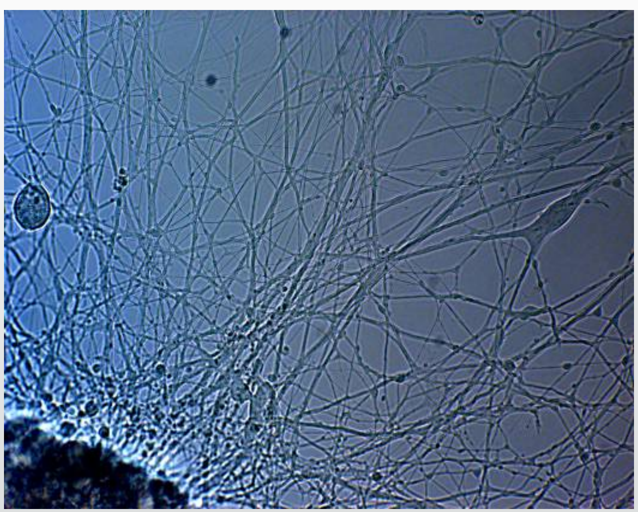
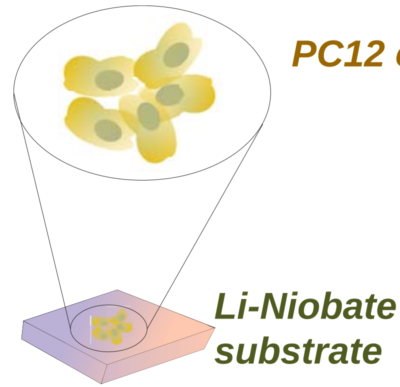
Intercepting Neural Signalling







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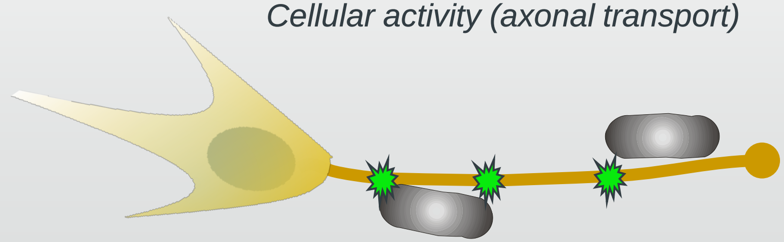

cell/neuritis-growth

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and Astronomy

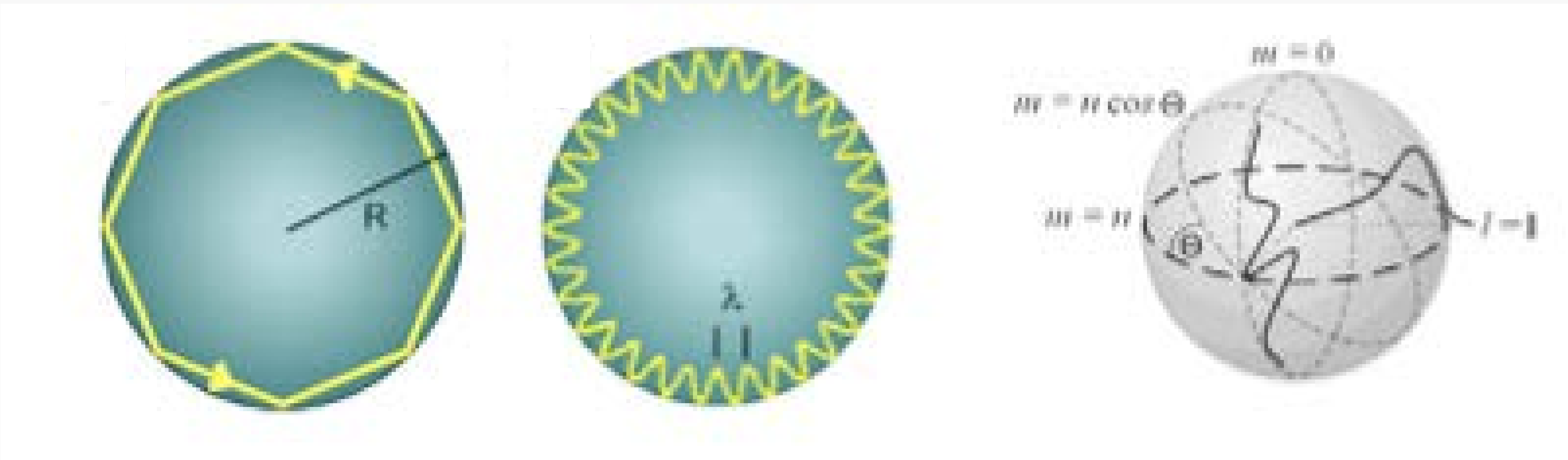
Single mode, single exciton lasing in NQRs

From the beauty of single quantum dot physics

to ensemble applications …

Whispering gallery mode resonators

Light confinement inside a microsphere



Geometric optic

Wave optic

Schematic of a spherical microcavity showing distribution and spatial orientation of the mode

Rakovich et al., Laser & Photon. Rev. 4, No. 2, 179–191 (2010)

Single-mode single-exciton Laser from quasi-type II Colloidal Quantum Rods

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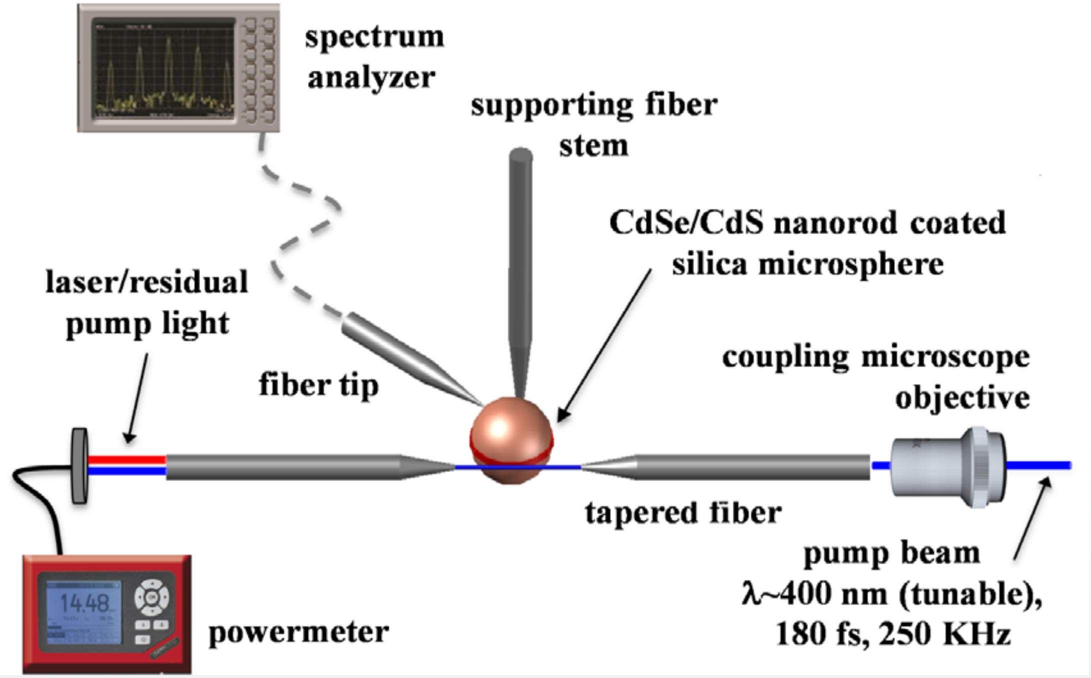
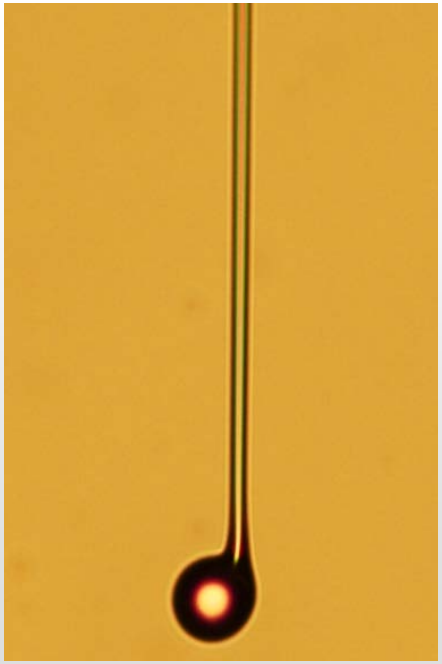
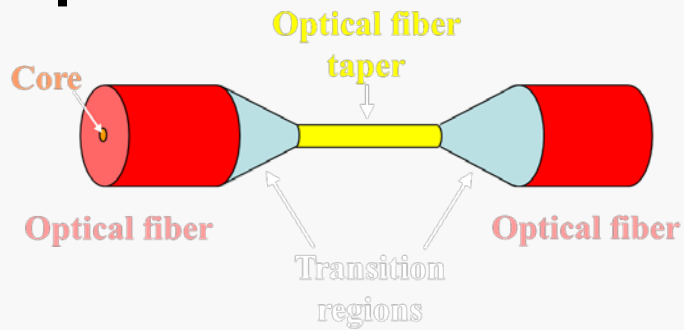


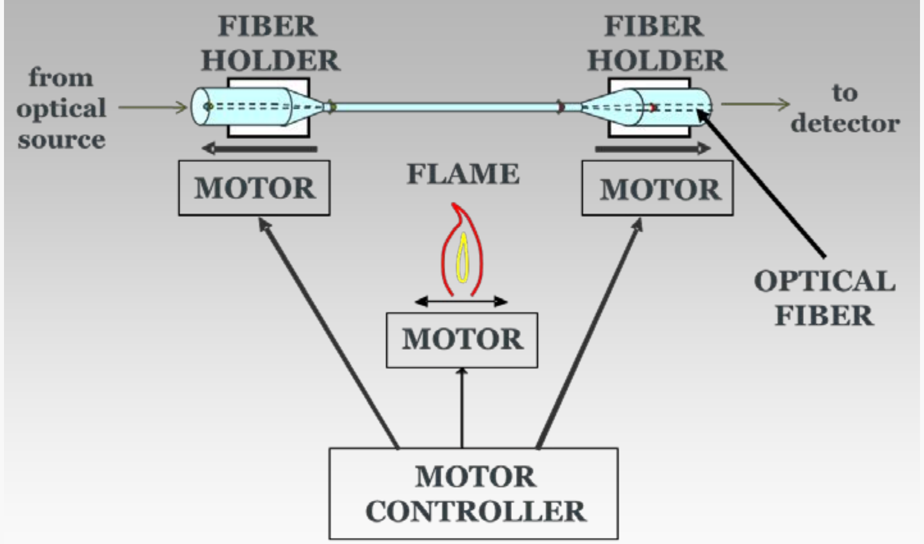
Schematic of the experimental arrangement used for demonstration of fiber-coupled laser operation of CdSe/CdS core/shell nanorods in silica microspheres.



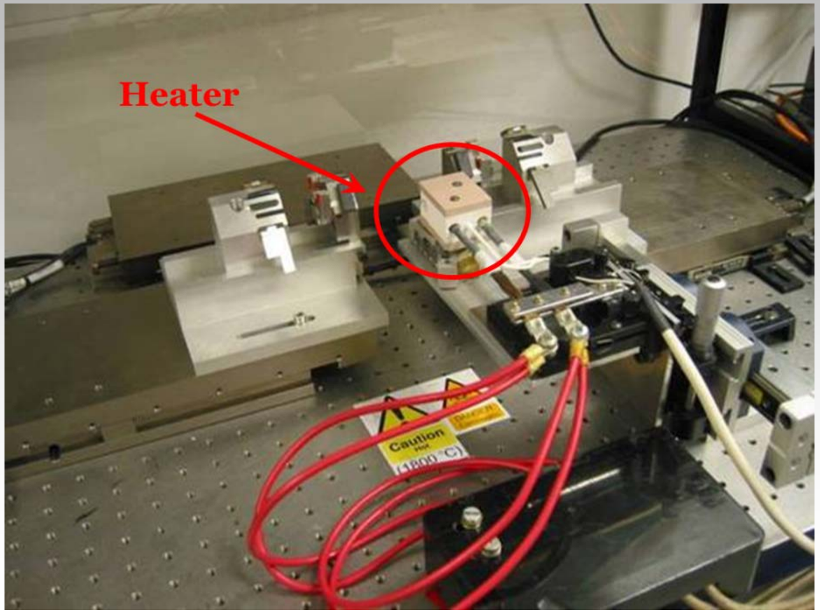
Fabrication procedures



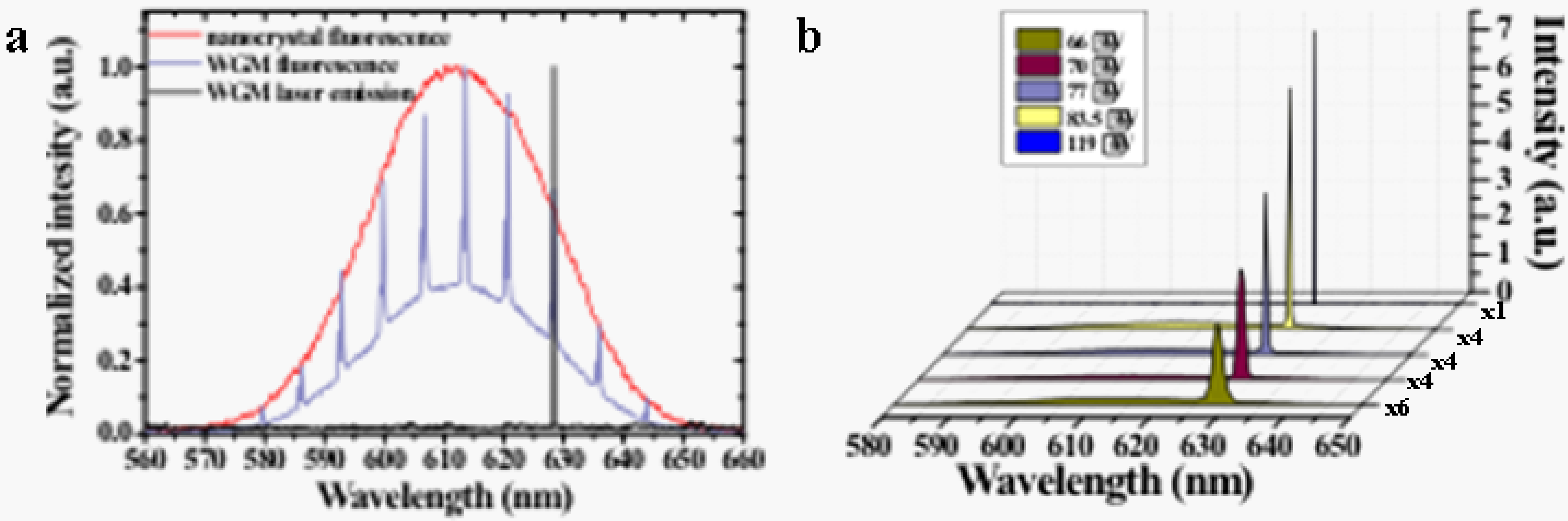
flame brushing technique



MODIFIED
flame brushing technique



Whispering gallery mode fluorescence



Single-mode laser emission:

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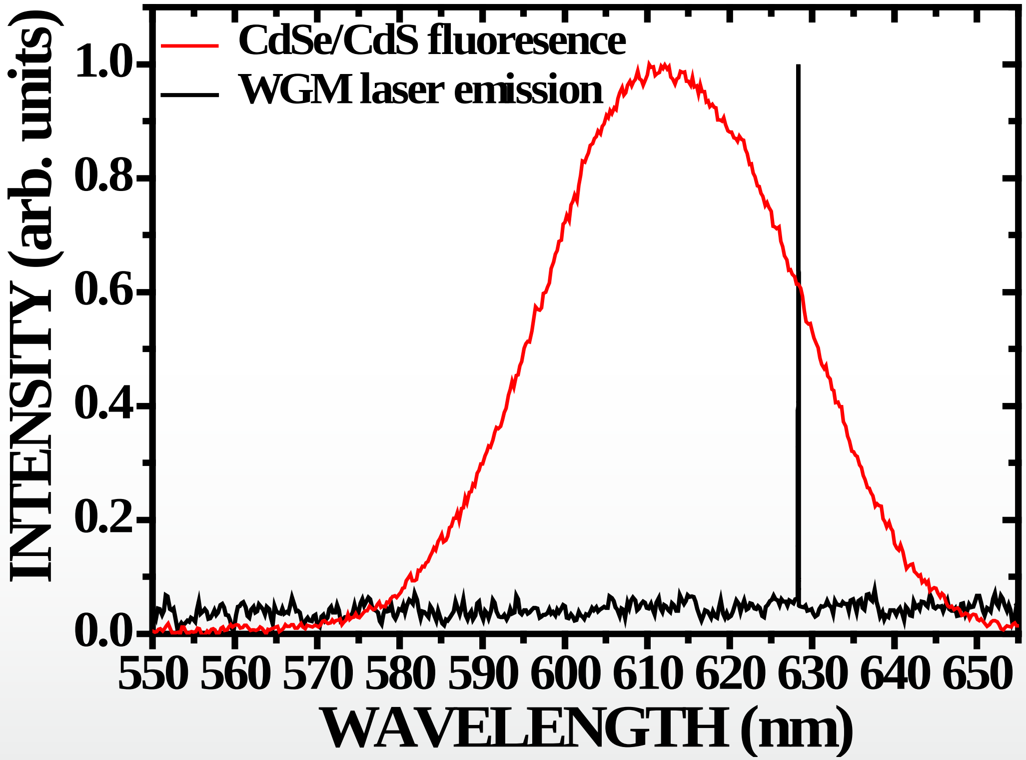

Laser (black line) and fluorescence emission (red line) spectra from a 9.2-μm-diameter hybrid sphere and the CdSe/CdS nanorods attached to the sphere, respectively.

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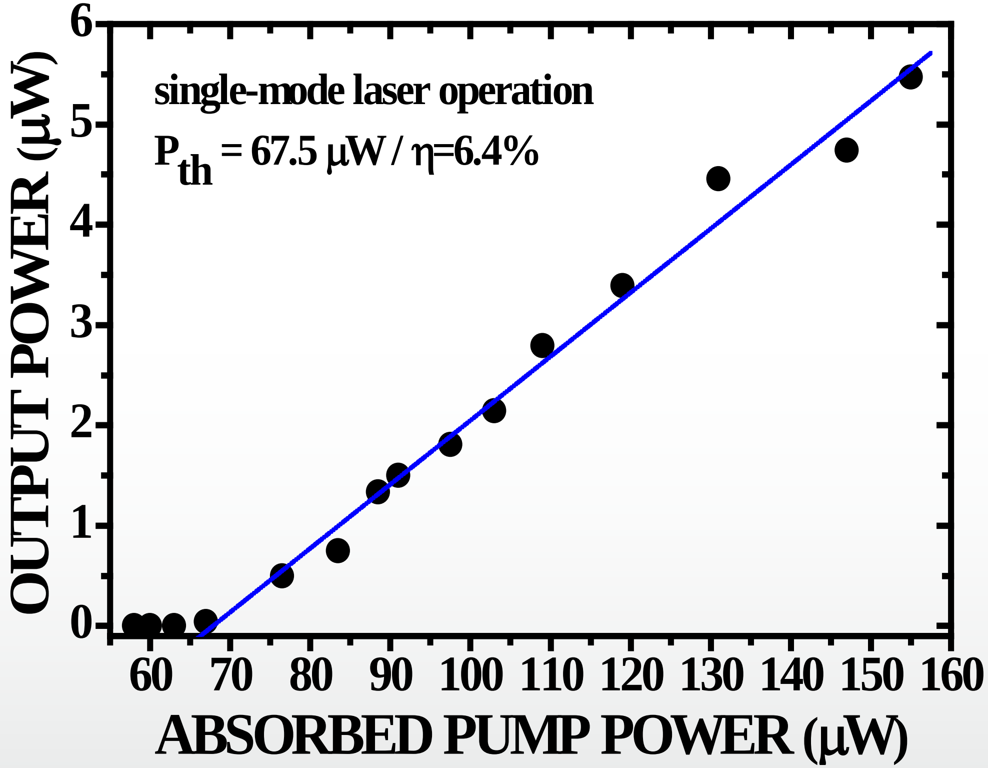
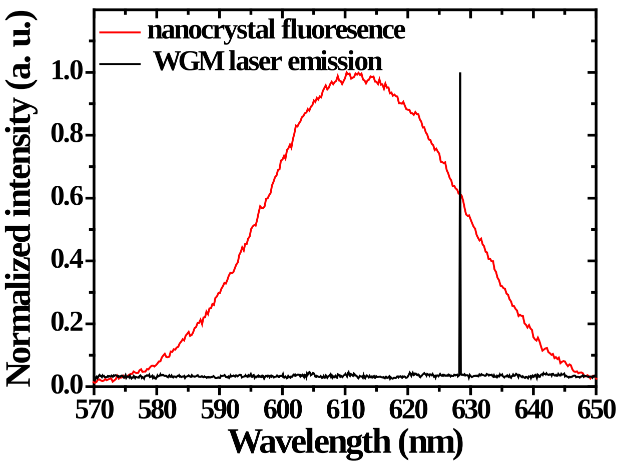
Output intensity vs absorbed power:

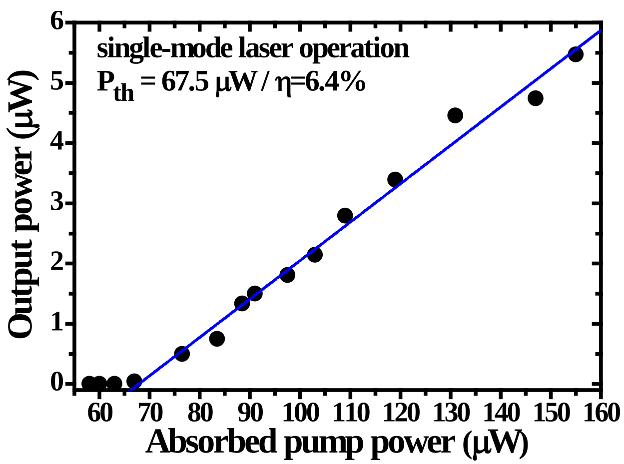


Laser output power as function of pump power for the single-mode laser operation of a 9.2-μm-large hybrid microsphere.

Single mode laser

UNIVERSITY OF Southampton





- ✓ Excitation in equatorial zone
- ✓ Microsphere diameter: 9.2 μm
- ✓ Q-factor after the coating 10^5
- ✓ Laser emission at 628.32 nm
- ✓ Laser line FWHM: 0.06 nm
- ✓ Lasing threshold: 67.5 μW
- ✓ Maximum output power: 5.5 μW
- ✓ Slope efficiency: 6.4%

Multimode laser emission

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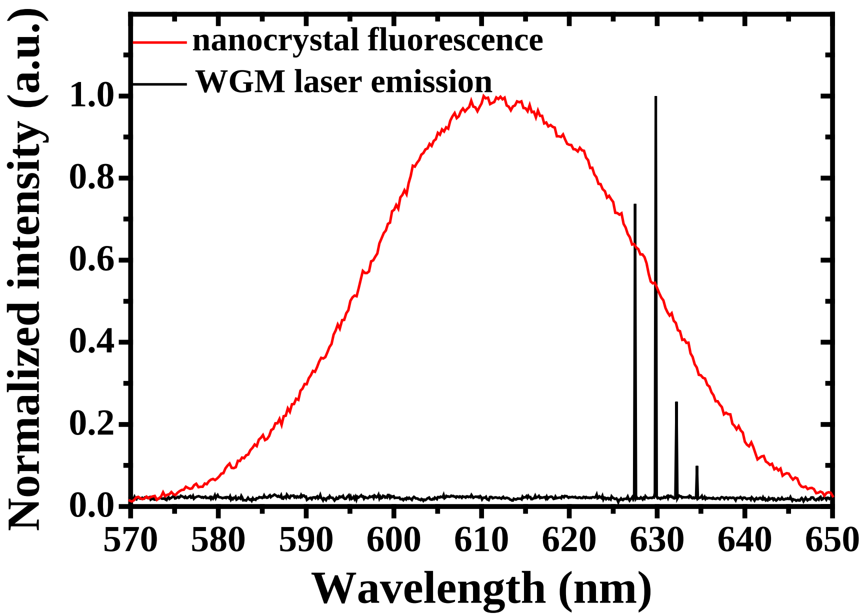
Microsphere diameter: 29.4 μm



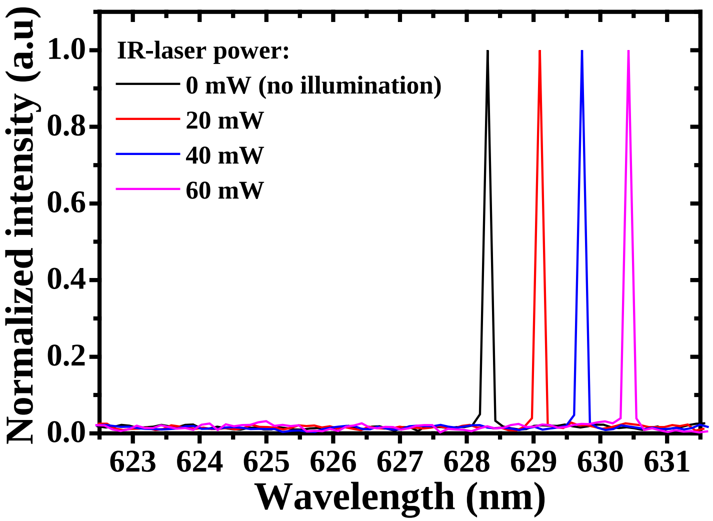
✓ The lasing modes distance: 2.4 nm.

Free spectral range

$$\Delta\lambda_{FSR} = \left(\frac{\lambda_L^2}{2 \cdot \pi \cdot R_H \cdot n_2}\right) \cdot \left(\frac{tan^{-1}\left[(n_s/n_{nc})^2 - 1\right]^{1/2}}{\left[(n_s/n_{nc})^2 - 1\right]^{1/2}}\right) = 2.375\ nm$$

Tunable laser emission

University of Southampton



- ❑ Heating of the microsphere with 3.5-μm fs laser (Rep. Rate 80MHz)
- ✓ Shift of laser emission 2.1 nm

Temperature variation of the microsphere:

$$\Delta T_c = \frac{P(1-R)}{2\sqrt{\pi}\omega_o \kappa_s}\left(1+\frac{\kappa_a}{\kappa_s}\right)^{-1}$$

Calculation of the tuning range:

$$\Delta\lambda = \lambda * a_{nc} * \Delta T + \lambda * a_s * \Delta T + \lambda * \frac{1}{n_{nc}} * \frac{dn_{nc}}{dT} * \Delta T + \Delta\lambda_{bg}$$

- thermal expansion of the CdSe/CdS nanocrystals
- thermal expansion of the silica microsphere template
- thermo-optic coefficient of the nanocrystals
- change of the CdSe bandgap

manuscript submitted to Nature Photonics

IR tuning of laser emission: model vs experiment

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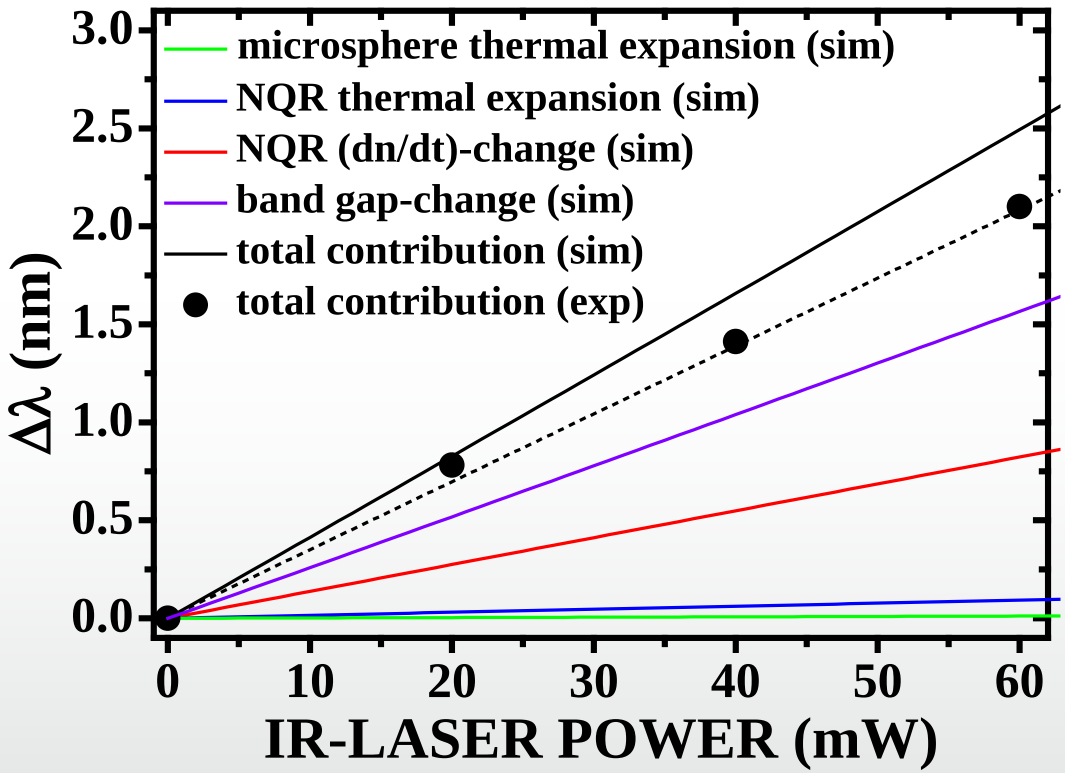
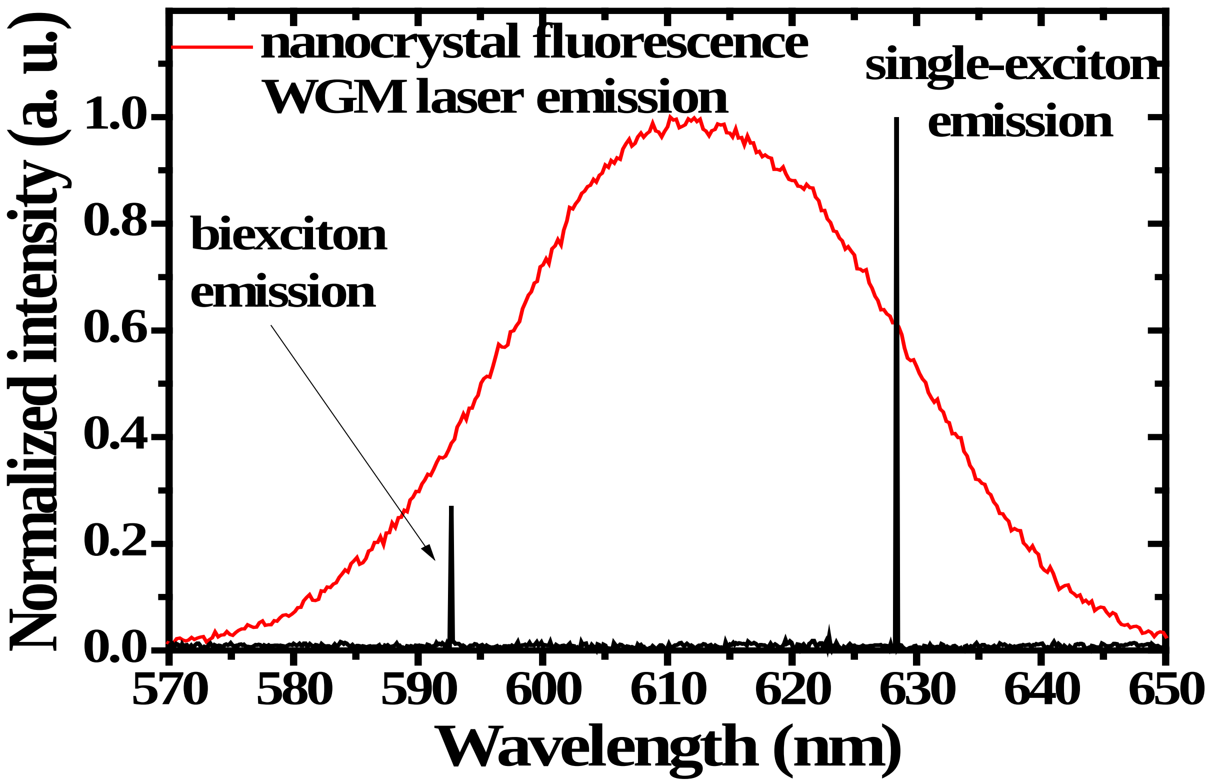
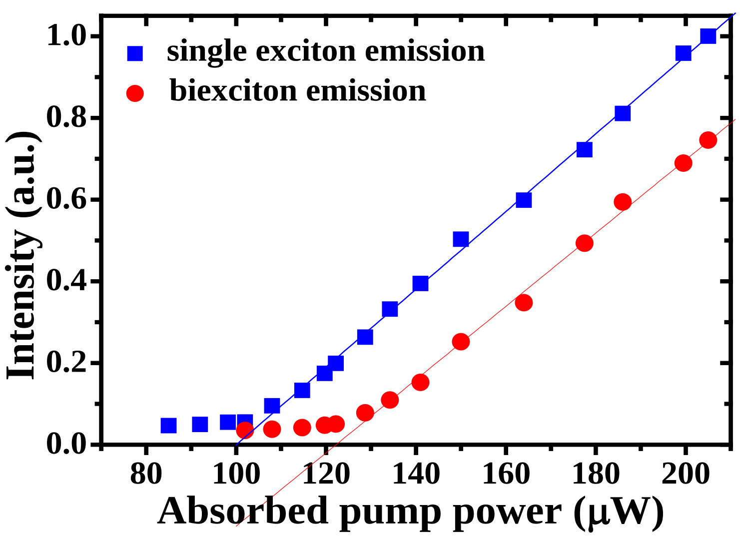


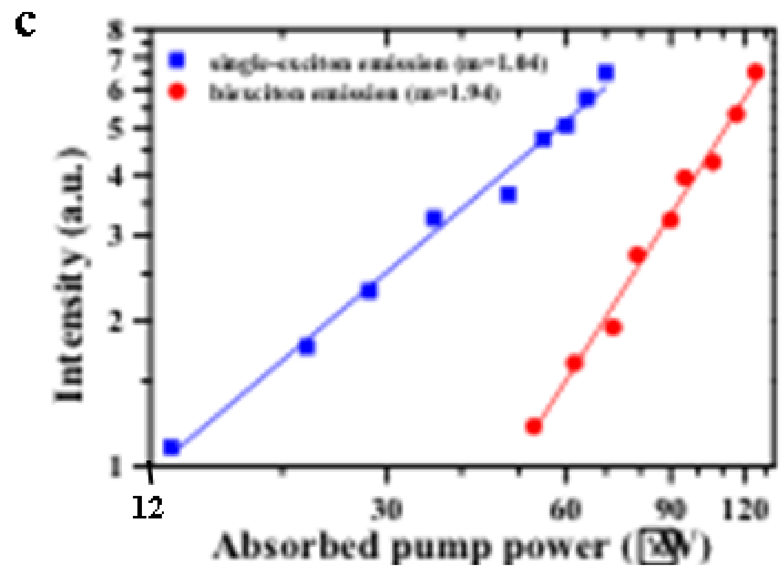
Multimode laser emission



- ✓ Excitation away from the equatorial zone
- ✓ Second laser line: 592.6 nm
- ✓ Pump power thresholds of 100 μW and 122 μW

Multimode laser emission





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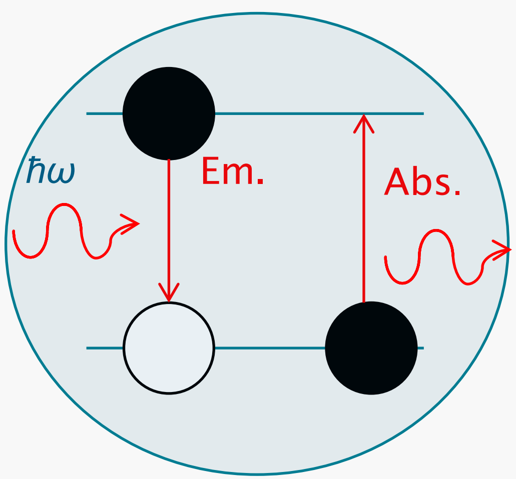
Vol 447 | 24 May 2007 | doi:10.1038/nature05839

nature

ARTICLES

Single-exciton optical gain in semiconductor nanocrystals

Victor I. Klimov[1], Sergei A. Ivanov[1], Jagjit Nanda[1], Marc Achermann[1], Ilya Bezel[1], John A. McGuire[1] & Andrei Piryatinski[1]



Transparenc
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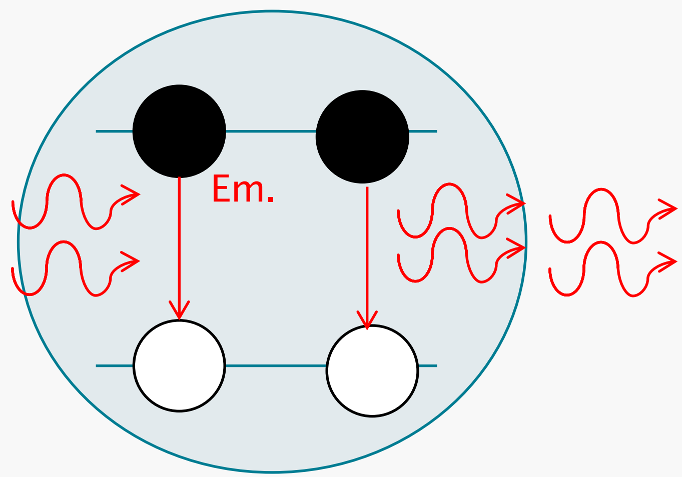
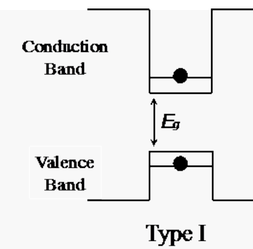


Population Inversion
Biexciton excitation
Biexciton gain mechanism

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ARTICLES

Single-exciton optical gain in semiconductor nanocrystals

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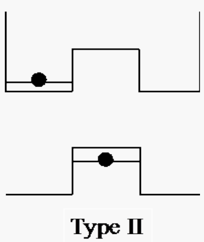
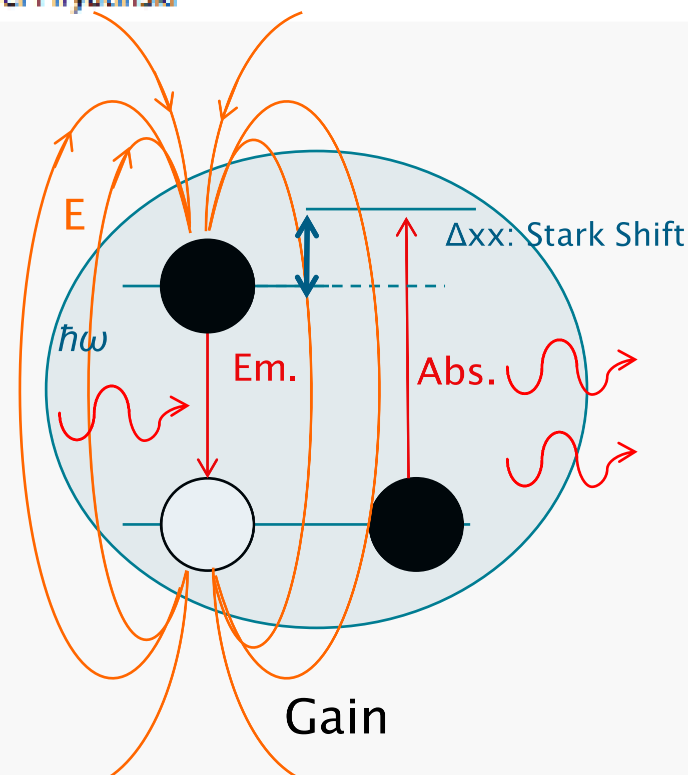




Stark Shift: $\Delta_{XX}=E_{XX}-2E_{X}$

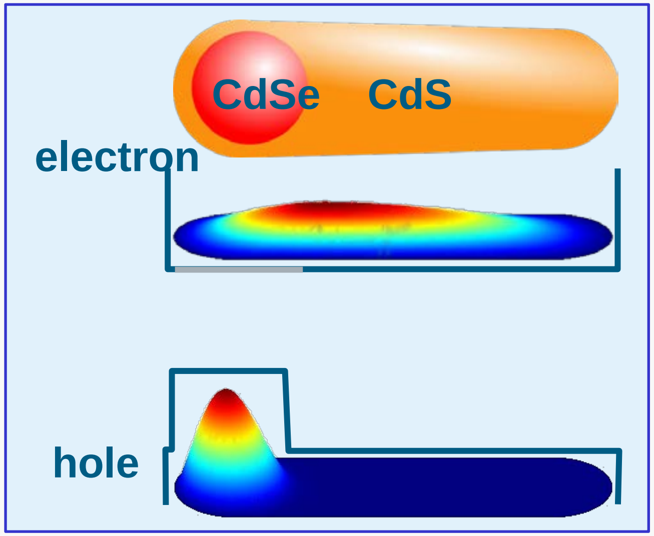
Charge density:

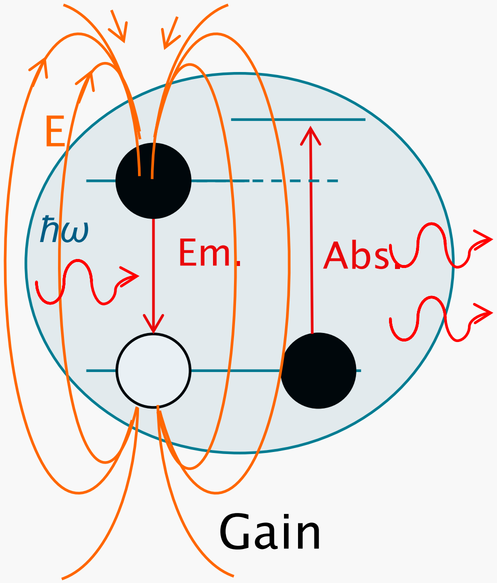
$\rho_X(r)=\rho_h(r)+\rho_e(r)$

$\rho_X(r)=e(|\Psi_h(r)|^2-|\Psi_e(r)|^2)$

Optical gain on CdSe/CdS QRs

Length: 27.7±2.2 nm
Width: 4.1±0.6 nm





Conduction band offset: ±0.3 eV
Valence band offset: 0.78 eV

$\rho_X(r)=e(|\Psi_h(r)|^2-|\Psi_e(r)|^2)$

Exciton dynamics in CdSe/CdS QRs

Calculation of the wavefunctions and energies of electrons and holes

$$\left[-\frac{\hbar^2}{2m_e^*}\nabla^2 + q_e(\Phi_h + V_{cb})\right]\psi_e = E_e\psi_e$$

$$\left[-\frac{\hbar^2}{2m_h^*}\nabla^2 + q_h(\Phi_e + V_{vb})\right]\psi_h = E_e\psi_h$$

$$\nabla^2\Phi_e = -\frac{\rho_e}{\varepsilon\varepsilon_o}$$

$$\nabla^2\Phi_h = -\frac{\rho_h}{\varepsilon\varepsilon_o}$$

$$\rho_e = q_e\frac{\psi_e^2}{\langle\psi_e|\psi_e\rangle}$$

$$\rho_h = q_e\frac{\psi_h^2}{\langle\psi_h|\psi_h\rangle}$$

The calculations have been done in collaboration with Dr. Chunyong Li

Exciton dynamics in CdSe/CdS QRs

UNIVERSITY OF Southampton

Single Exciton:

$E_e=0.14876$ eV-- $E_h=0.143949$ eV

$E_x=E_e+E_h+E_g=1.972$ eV

➔ $\lambda_x=$ 628.5 nm

Biexciton:

$E_{e1}=0.15162$ eV-- $E_{h1}=0.19835$ eV

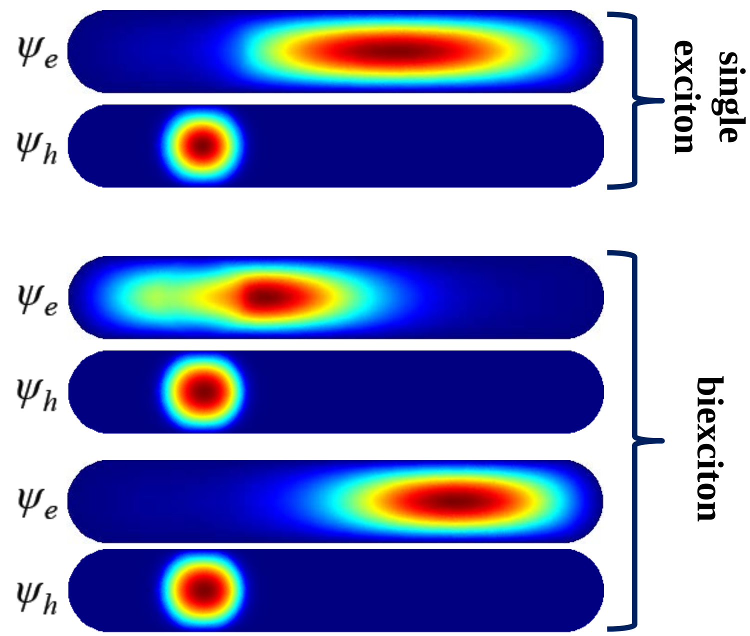
$E_{e2}=$ 0.15363eV-- $E_{h2}=0.19835$eV

$E_{xx}=E_{e1}+E_{h1}+E_{e2}+E_{h2}+2*E_g=$ 4.06195 eV

Stark Shift:

$\Delta_{xx}=E_{xx}-2*E_x=0.116532$ eV

➔ $\lambda_{xx}=$ 593.44 nm



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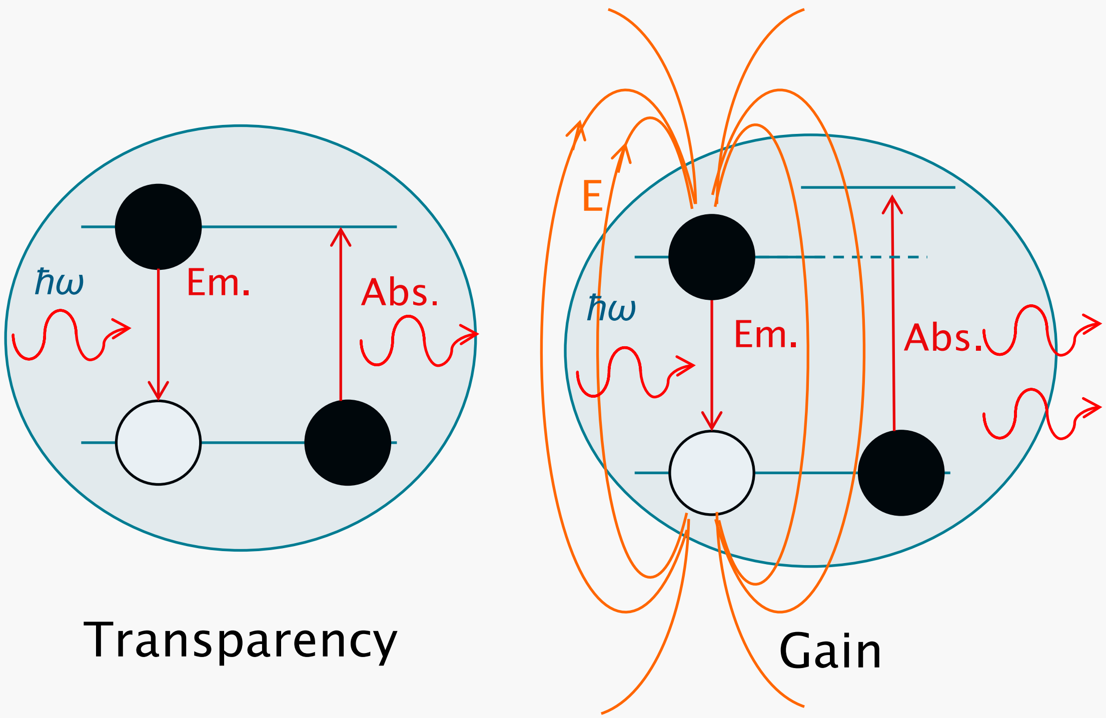
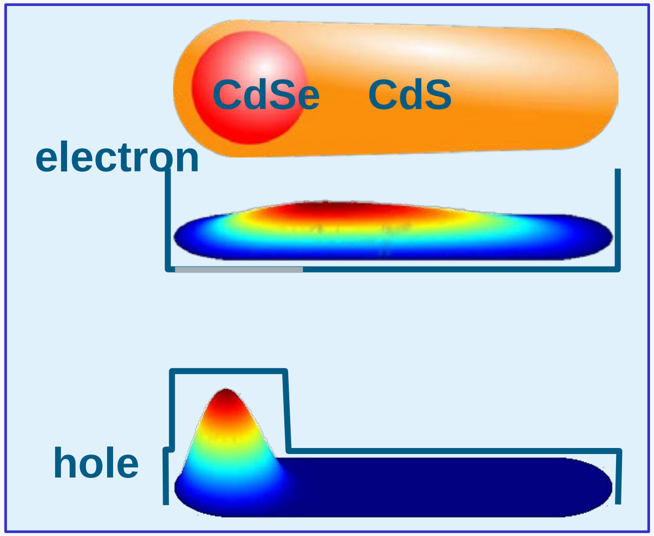
Optical gain on CdSe/CdS QRs



$$\rho_X(r) = e\,(|\Psi_h(r)|^2 - |\Psi_e(r)|^2),$$

Length: 27.7±2.2 nm
Width: 4.1±0.6 nm



Conduction band offset: ±0.3 eV
Valence band offset: 0.78 eV

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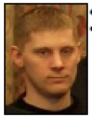

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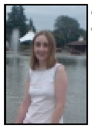

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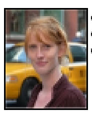

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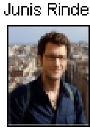

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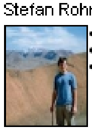

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