Sub-picosecond transient absorption of PbS nanocrystals on gold

Dario Grimaldi

Nanooptics Group, Department of Experimental Physics, Institute of Physics,
University of Graz, Austria

DocDay

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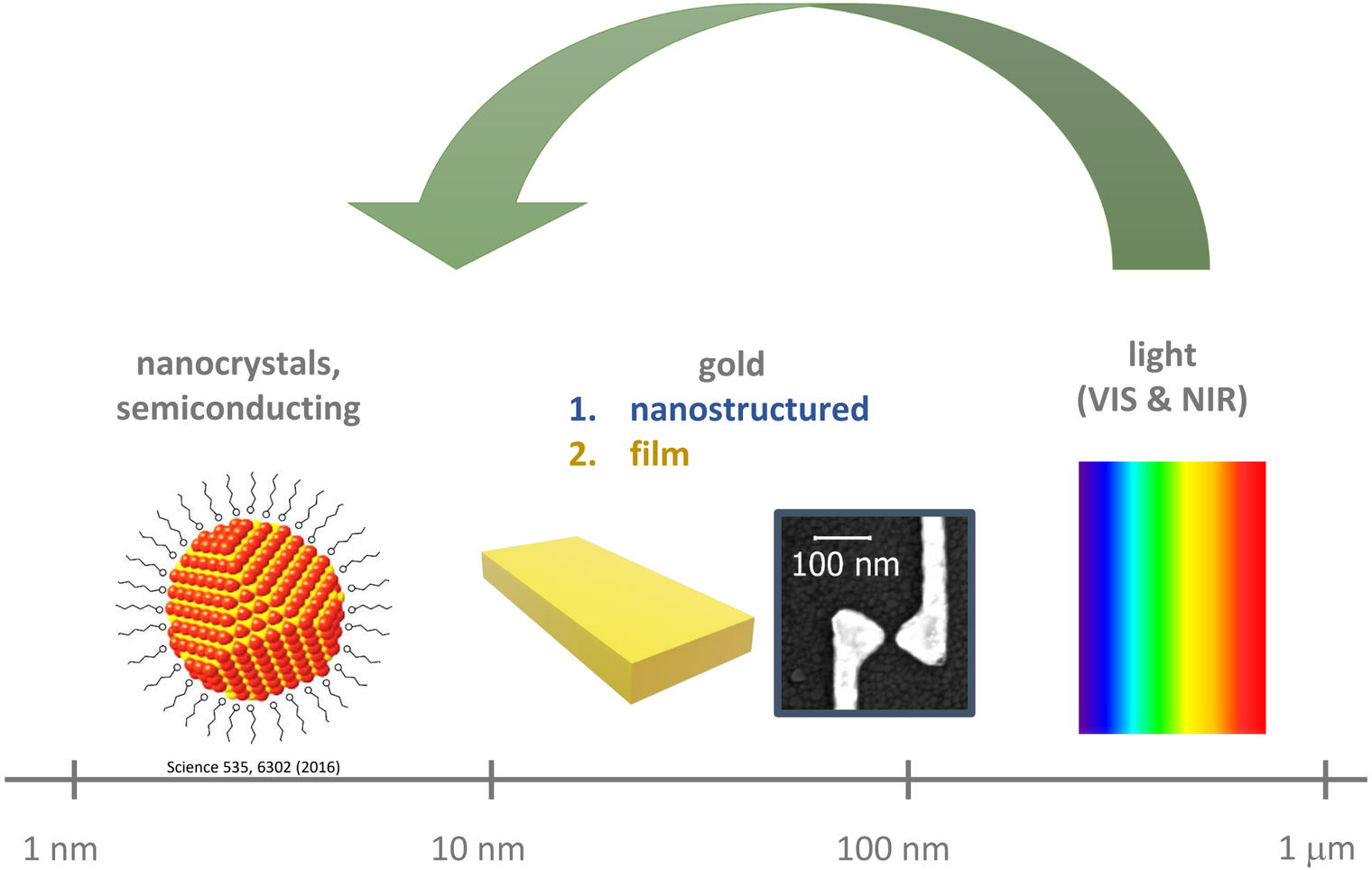
Premise

Nano scale

Investigation of

- optoelectrical (photoconductivity) &
- optical properties (transient absorption)



Outline

Introduction & Motivation

Lithographic nanogaps with few colloidal quantum dots (QDs)

Hybrid **film system** of **gold** with QDs

Method(s) & Sample(s)

Scanning **Photocurrent** Microscopy

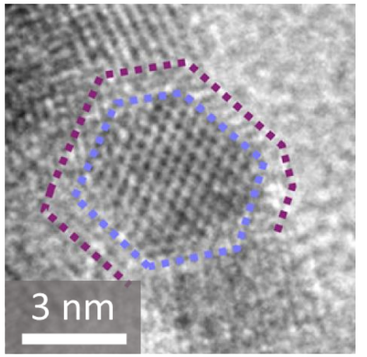
Ultrafast **Transient Absorption** Microscopy

Results & Discussion

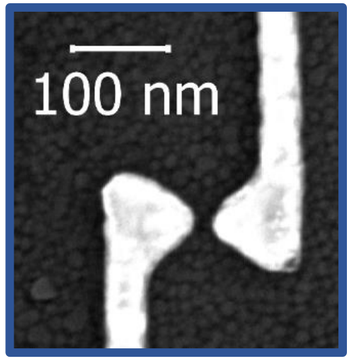
Photoconductivity at nanogaps & **I(P) power law dependence**

Sub-picosecond dynamics at the hybrid system

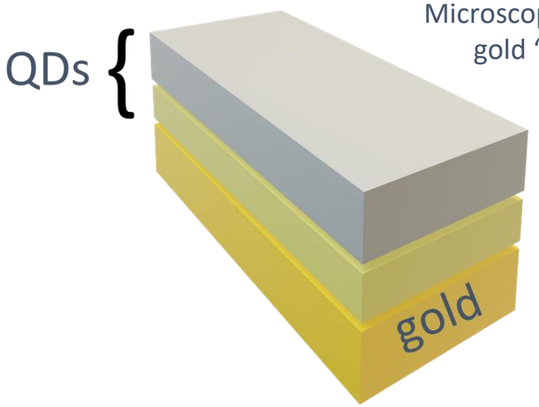
Summary, Outlook & Acknowledgements



Transmission Electron Microscopy image of a nanocrystal (QD)

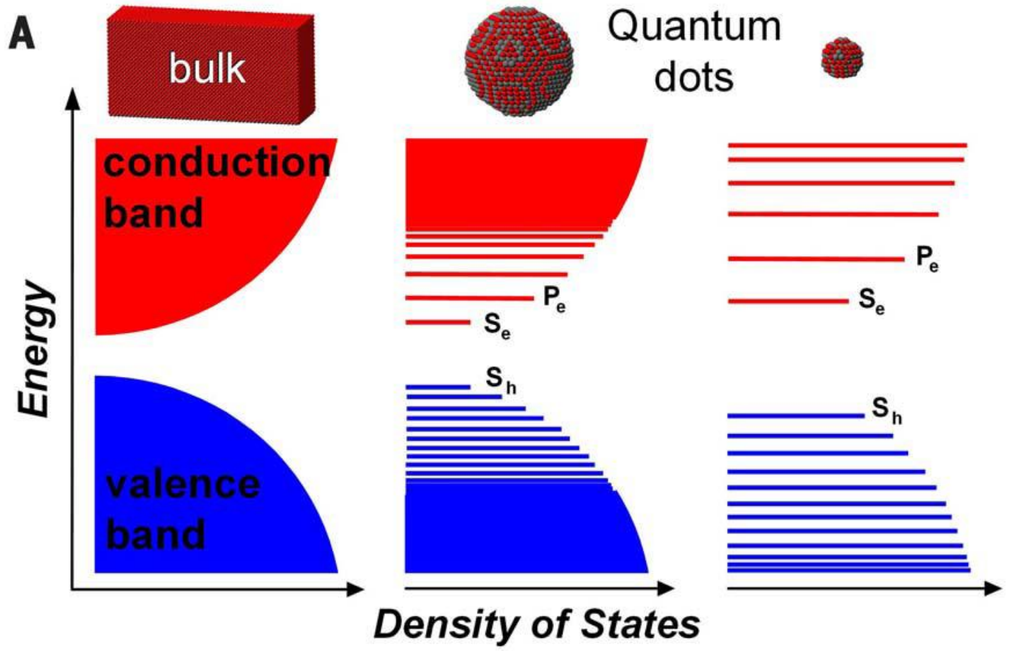


Scanning Electron Microscopy image of a gold “bow tie”



Optical properties of quantum dots

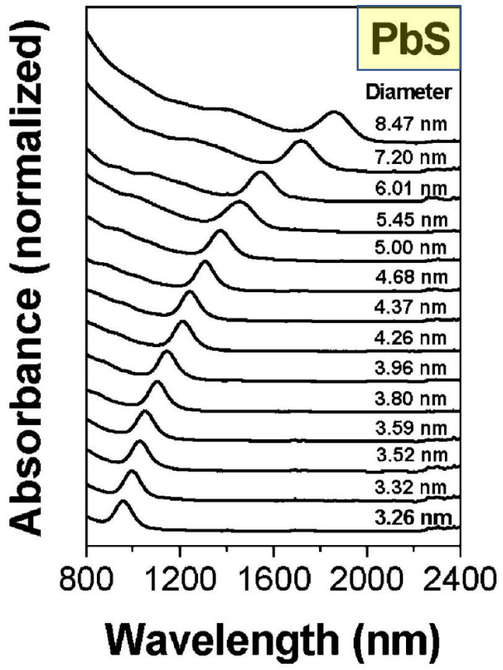
quantum confinement effect



discretization of near band gap states and band gap widening, **image taken from: C. R. Kagan et al.,** Science 535 6302 (2016)

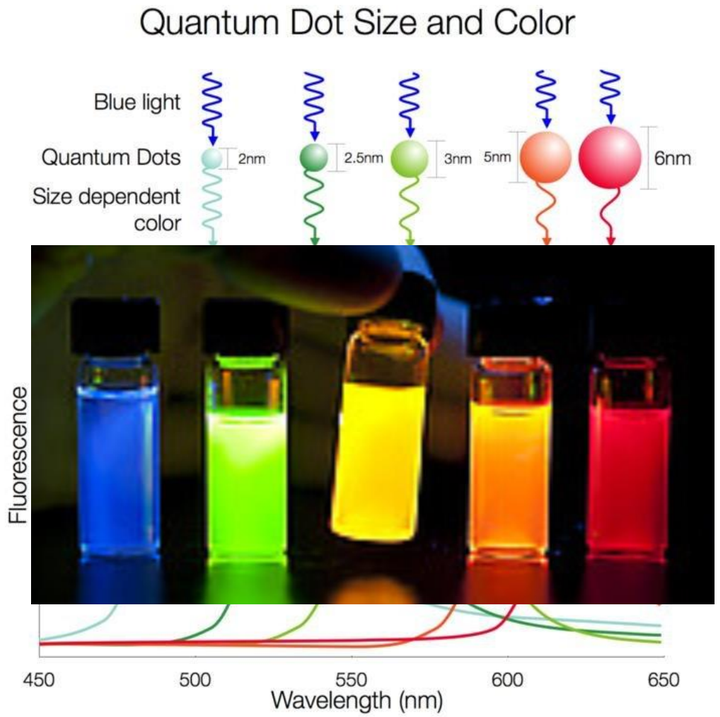
spectral tunability …

… in absorption



Spectral tunability of PbS QDs, **image taken from: J. Jasieniak et al .**, ACS Nano 5(7) 5888-902 (2011)

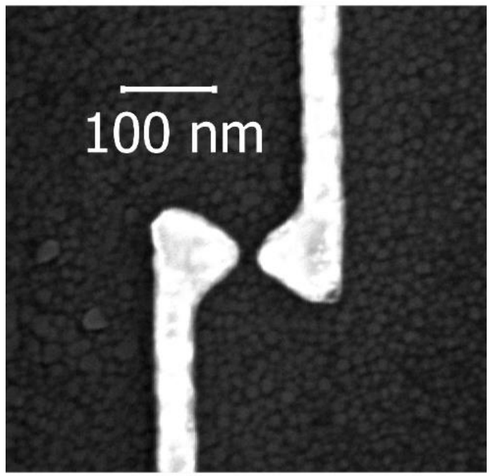
… and emission



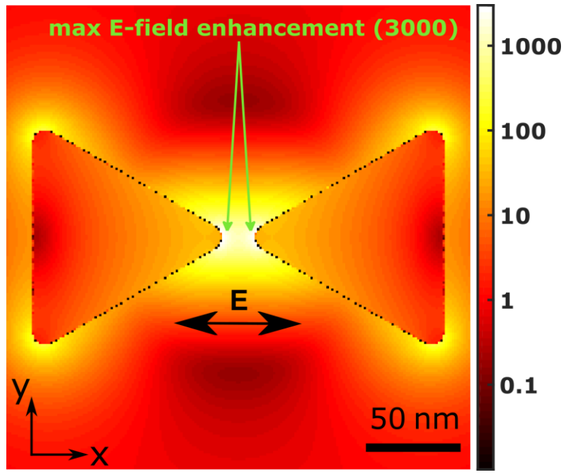
Light emission of **CdSe** QDs in dependence of the QD size, **Anton Paar**

Photoconductivity: Enhanced E-field at a plasmonic gap

tailored nanostructures, plasmonic gap electrodes



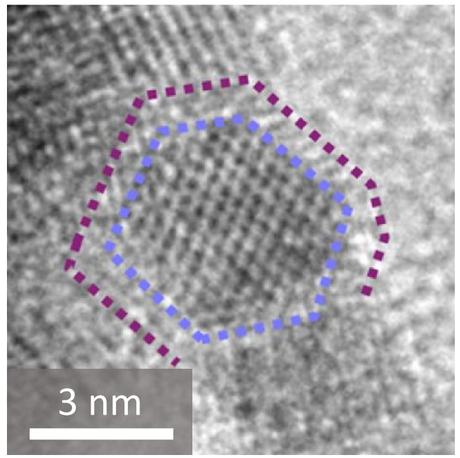
SEM (scanning electron microscopy) image of a lithographic Au bow tie gap electrode



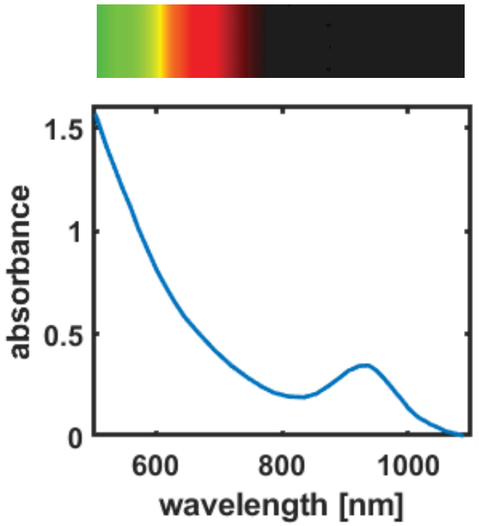
Near field enhancement of a bowtie simulated with the MNPBEM toolbox

~ 1 mln. times larger

semiconducting nanocrystals, PbS-$MAPbI_3$ quantum dots (QDs)



TEM image of a PbS-$MAPbI_3$ nanocrystal, **image taken from: Z. Yang et al.,** Nano Lett. 15, 7539 (2015)



Spectra of initial samples capped with oleic acid; in solution, before ligand exchange

Dario Grimaldi, dario.grimaldi@uni-graz.at

Charge carrier generation and transport in quantum dots

electron-hole pairs & trap states

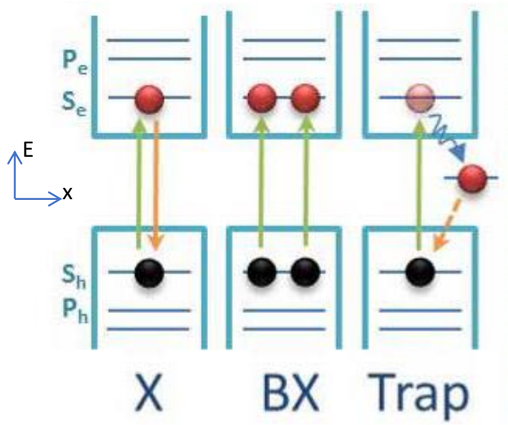
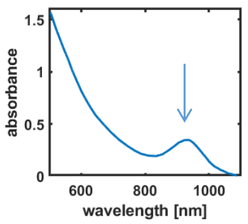


Image taken from: C. R. Kagan et al.,
Science 535 6302 (2016)



hopping transport

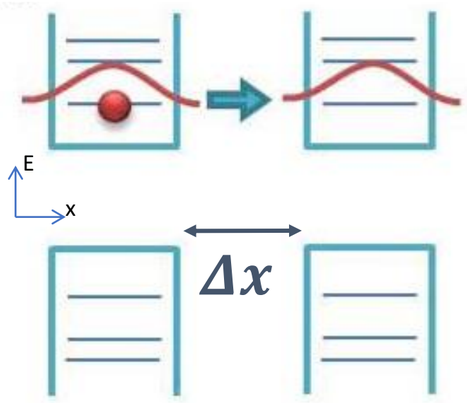
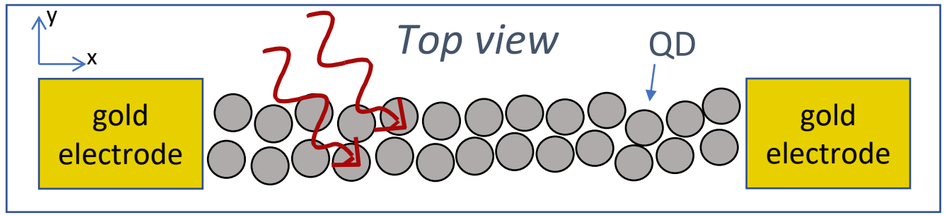
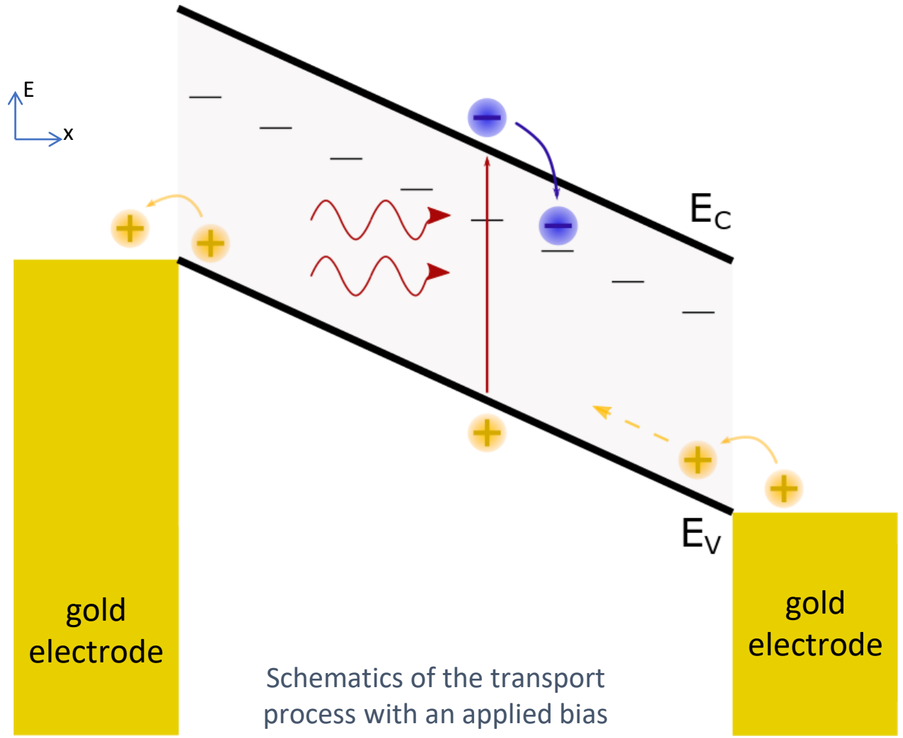


Image taken from: C. R. Kagan et al.,
Science 535, 6302 (2016)

tunneling rate of charge carriers:

$$\Gamma \sim \exp[-(2m^*\Delta E/\hbar^2)^{1/2}\Delta x]$$





Schematics of the transport process with an applied bias

Electron Beam Lithography, sample

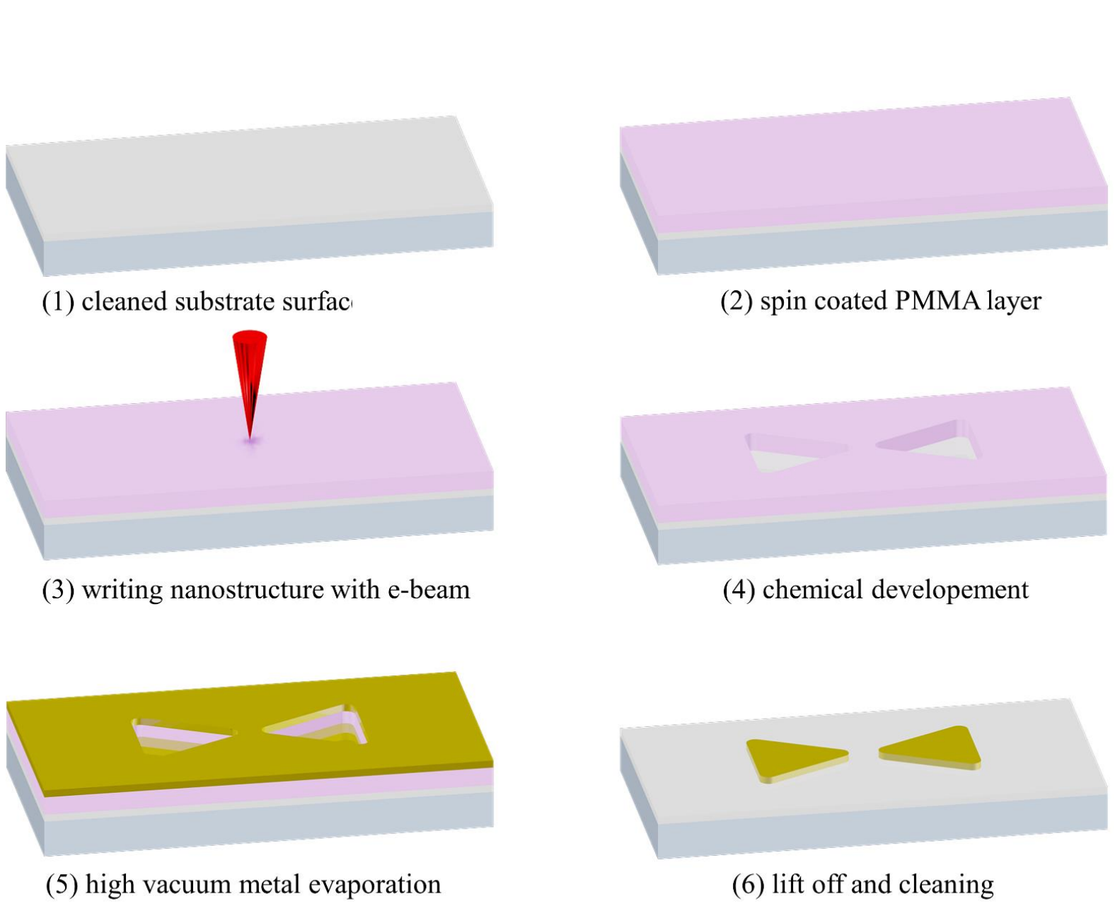
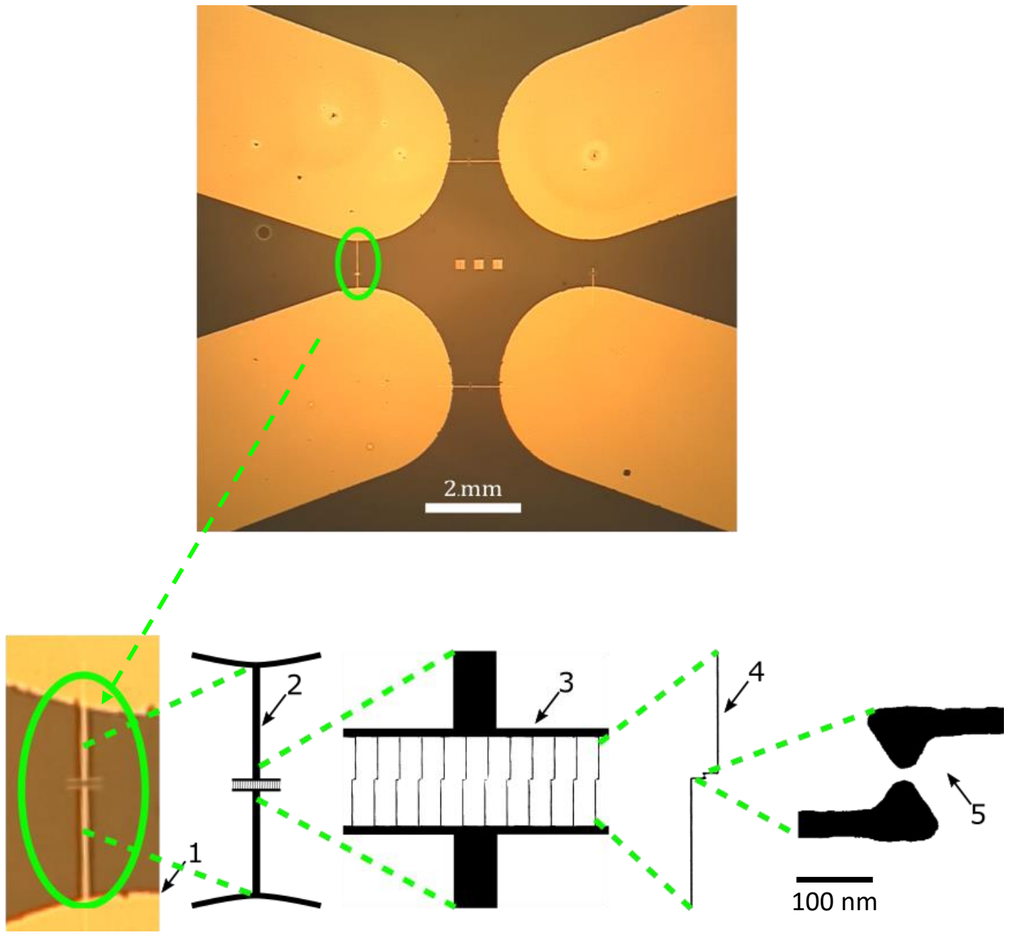


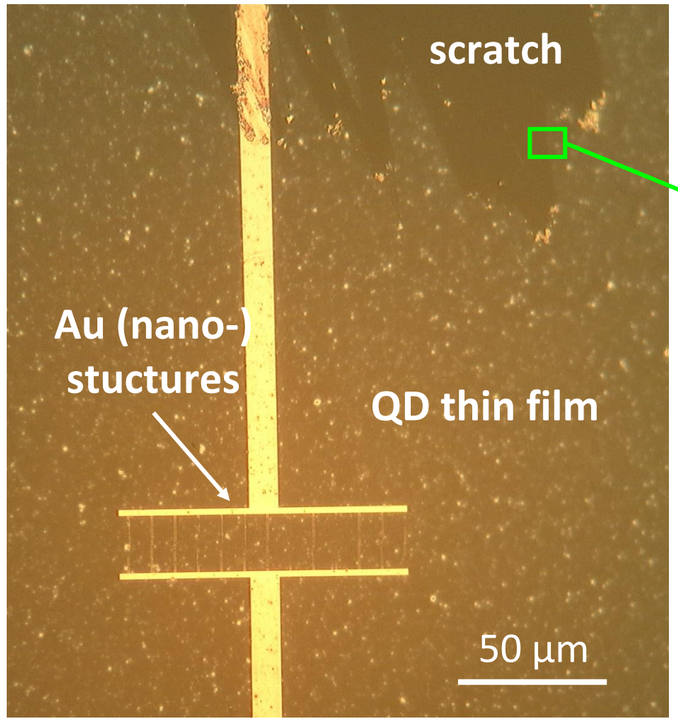
Image taken from: A. Trügler, Optical properties of metallic nanoparticles (2016)



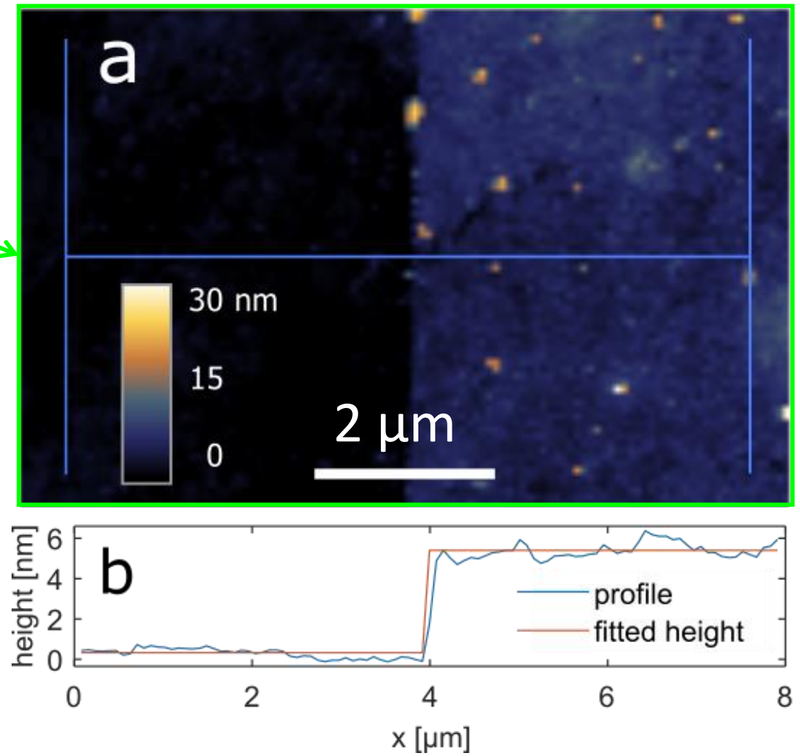
Optical microscope reflection image & illustration of the different EBL writing layers:
1. contact pads; 2. conducting paths, 3. cond. bars, 4. cond. rods, 5. bow tie electrode gap;

Quantum dots monolayer

spin coating ➡ thin film of QDs ➡ thickness determination w/ **atomic force microscopy**

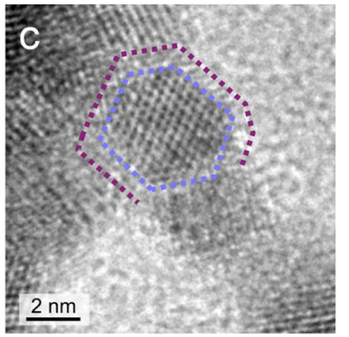


Light Microscope (reflection) image of the lithographic gold structures with QDs on top



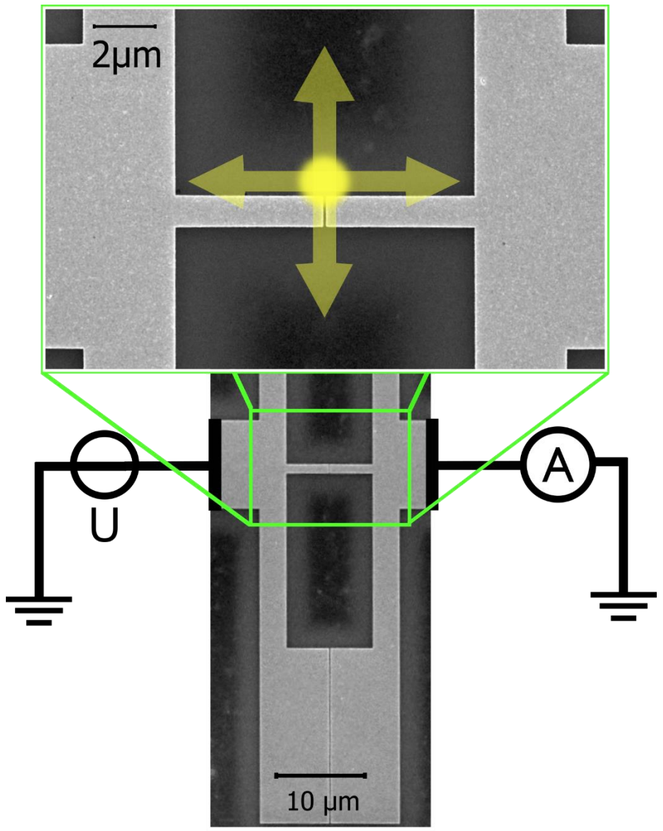
Atomic Force Microscopy image of the QD monolayer

5 nm ≈ 1 monolayer of QDs

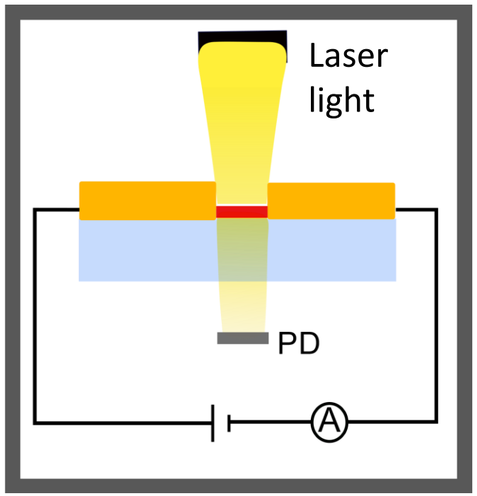


Scanning PhotoCurrent Microscopy (SPCM)

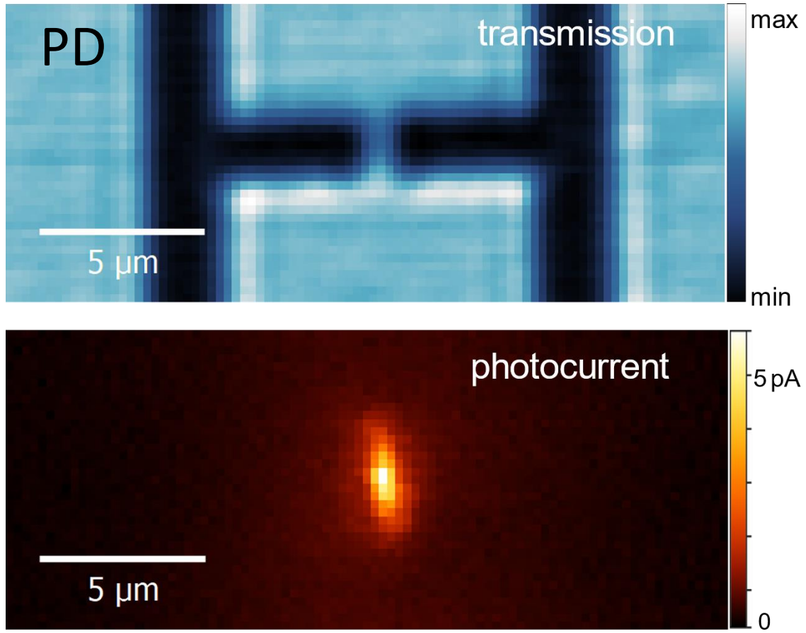
Top view

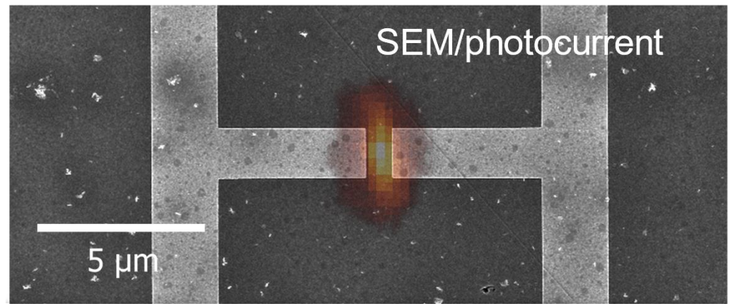


Side view



- bias source and ammeter
- λ-tunable laser, focused ($d_B \approx 1$ µm)
- photodiode (behind the sample)
- piezo scanning stage

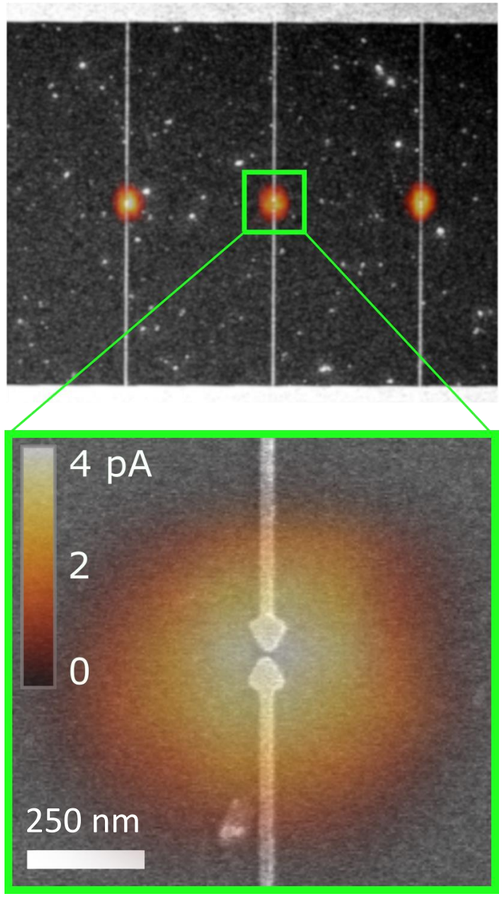




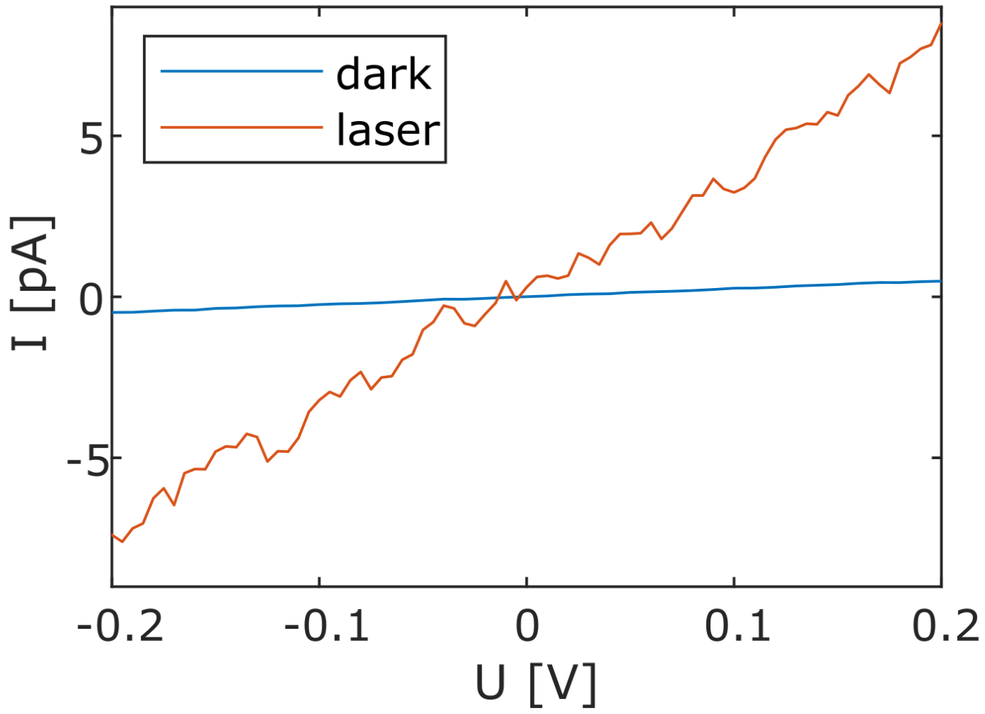
SPCM overlapped to a SEM image

SPCM at bow ties and I-V curve

Scanning PhotoCurrent Micrograph (overlapped to a SEM image) at bow tie nanogaps with only few QDs contributing to the photocurrent

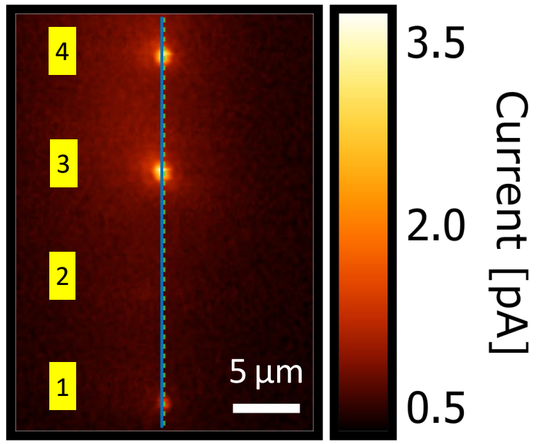


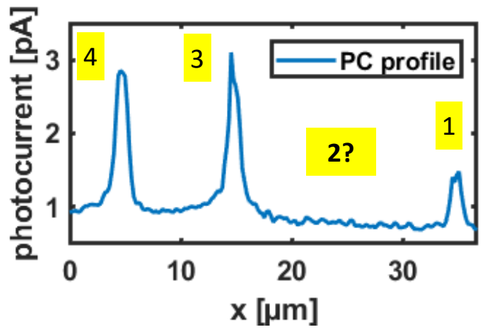
I-V curve off (dark) and on spot (laser)



Photoconductivity: Ultrasmall active area

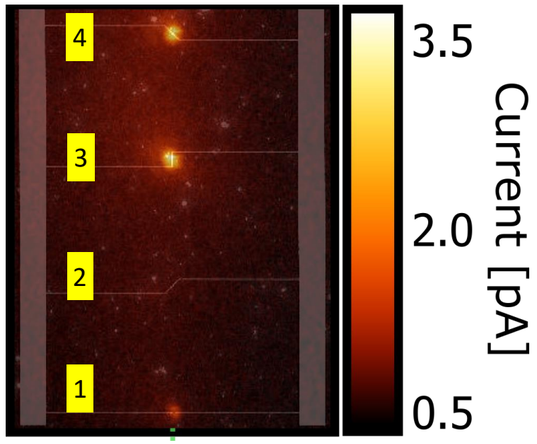
SPCM, profile



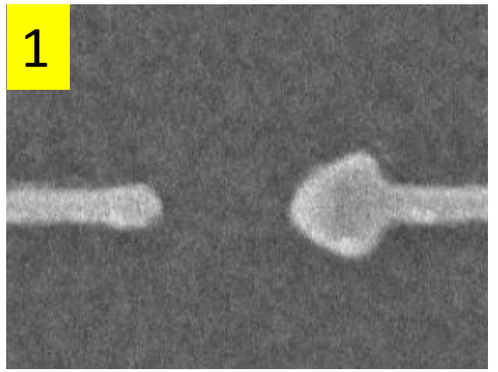


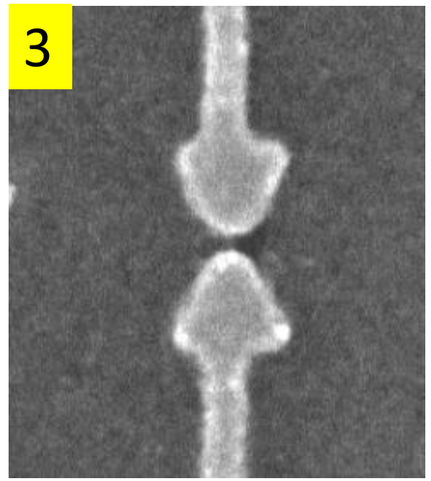
profile from top to bottom

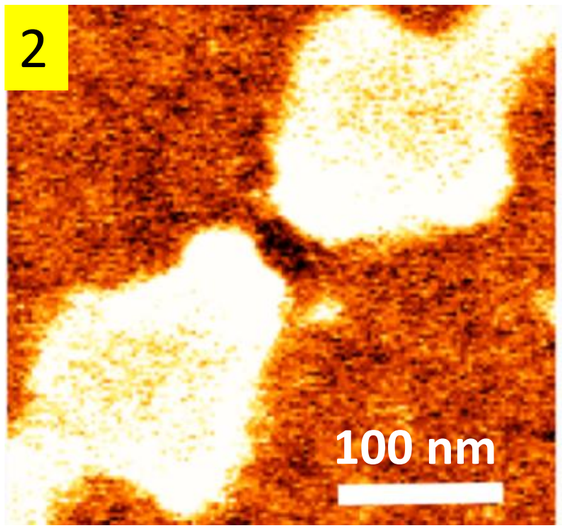
SPCM overlapped to SEM image of the same region

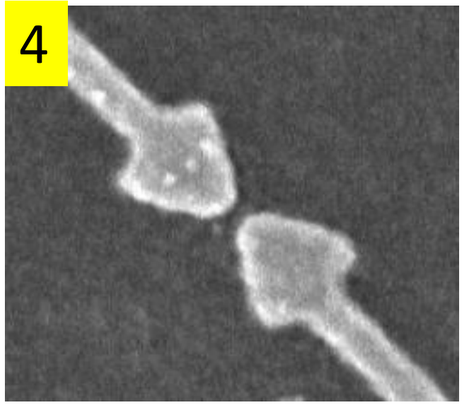


SEM analysis shows lack of QDs at a small 40x40 nm^2 region of bowtie 2

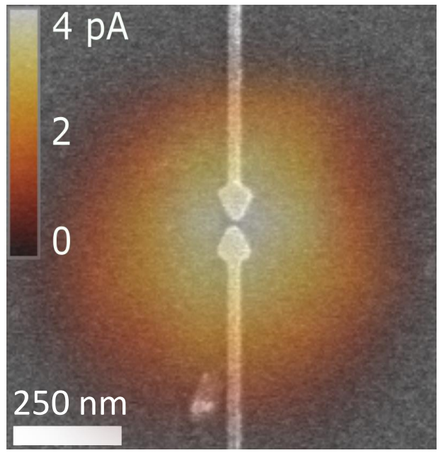




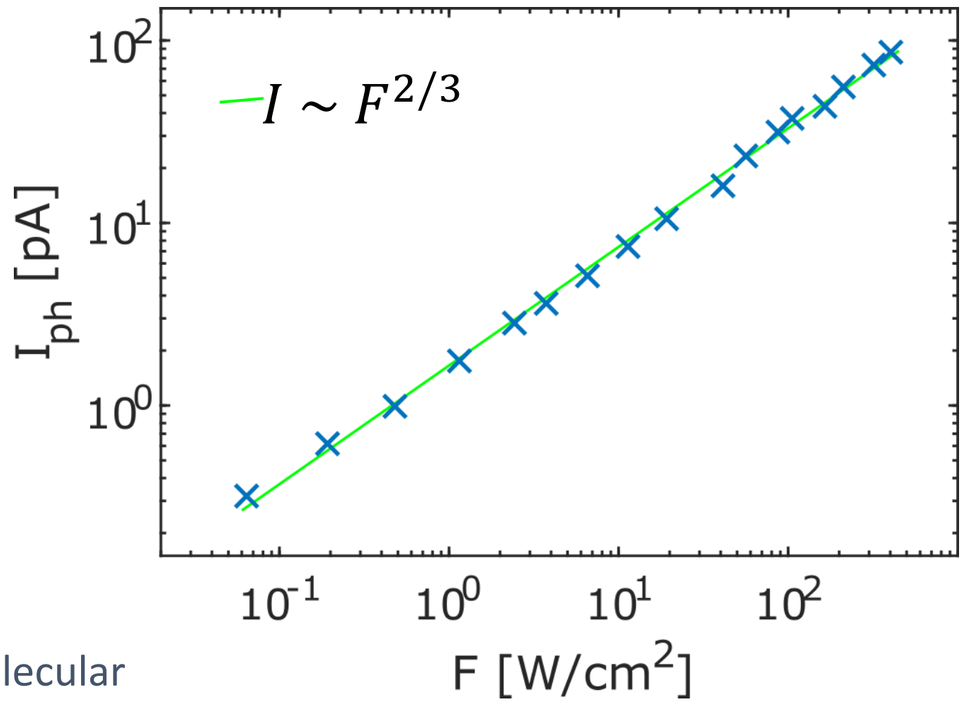




Photoconductivity: power law



photocurrent power law dependence
on the laser irradiance

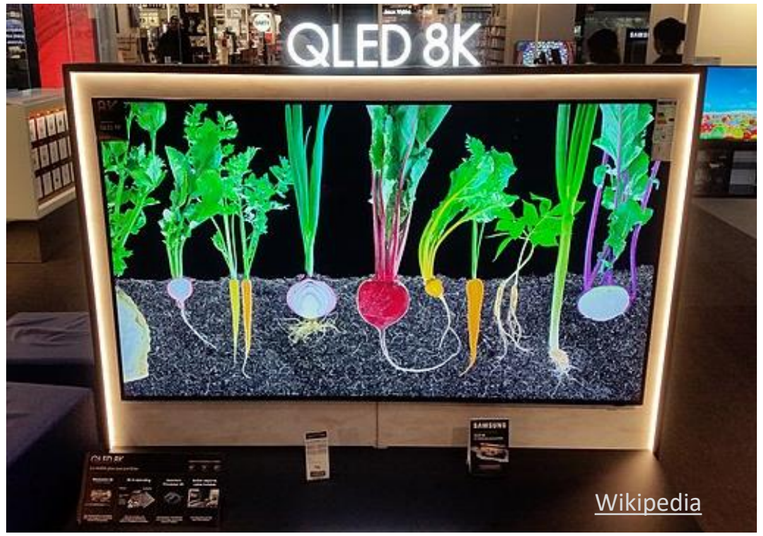


interpretation: mono- & bimolecular
recombination theory

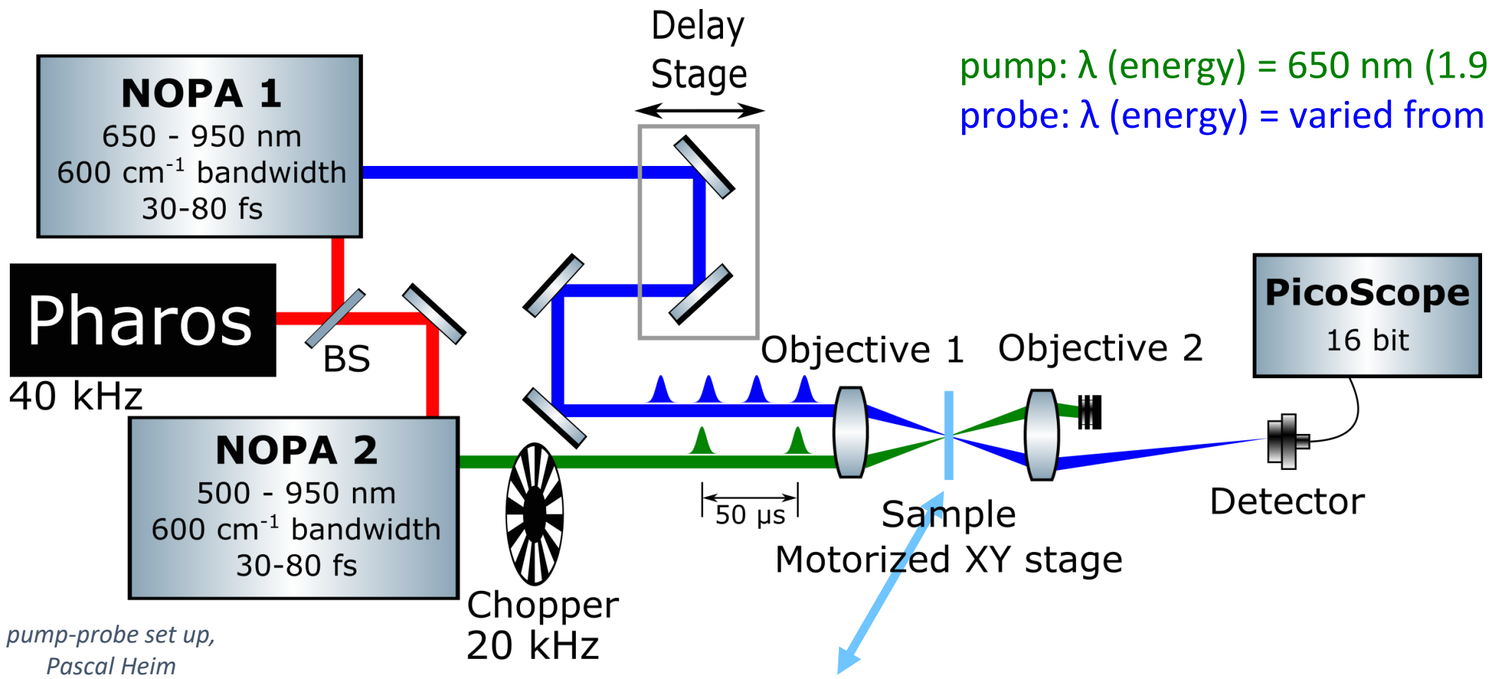
Dario Grimaldi, dario.grimaldi@uni-graz.at

Ultrafast Transient Absorption Microscopy: motivation

translucent **gold film (30 nm)** with a **QD film (5-100 nm)** on top,
possible applications:
photovoltaics and QLED displays

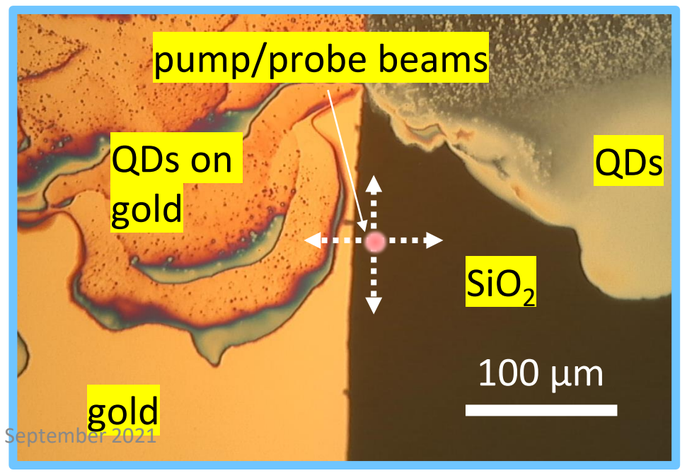


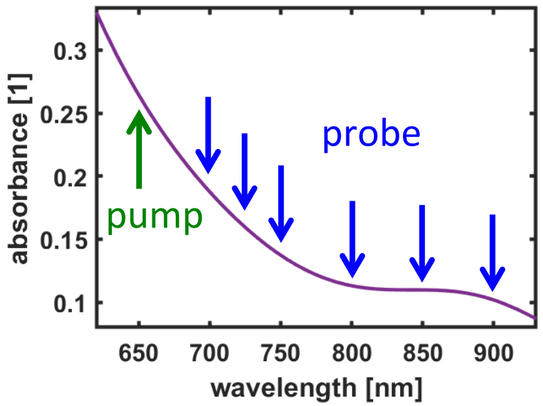
Ultrafast Transient Absorption Microscopy set up



pump-probe set up, Pascal Heim

pump: λ (energy) = 650 nm (1.91 eV)
probe: λ (energy) = varied from 700 nm (1.77 eV) to 900 nm(1.38 eV)





Transient Absorption Contrasts

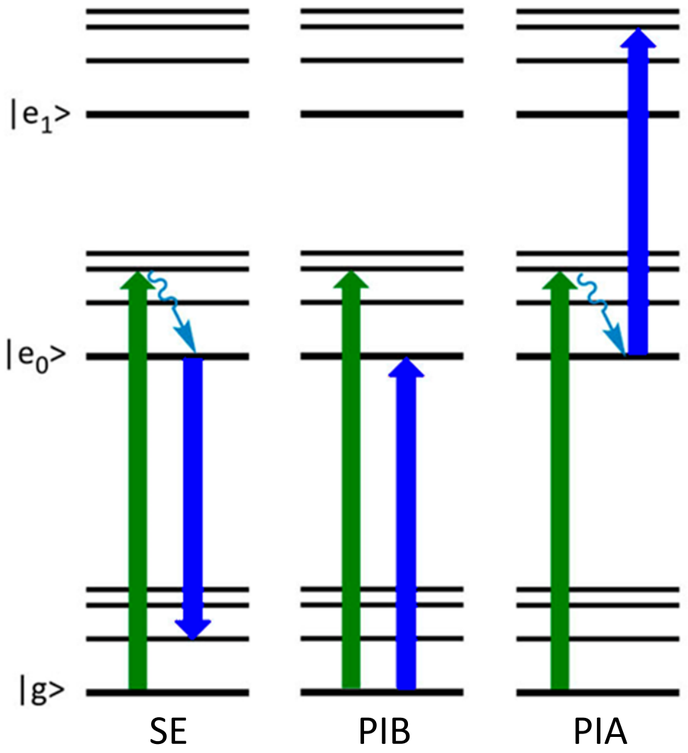
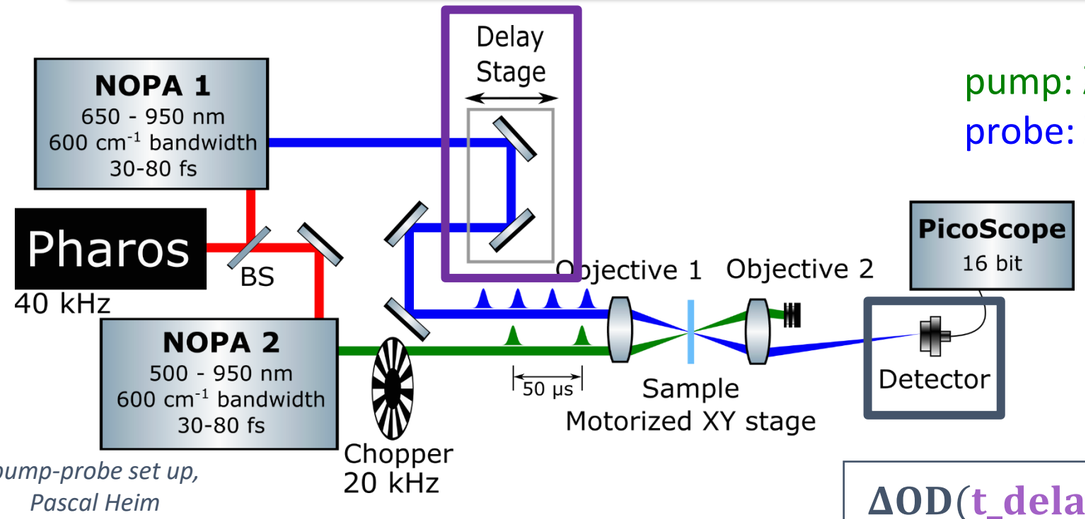


***Image adapted from**: Y. Zhu et al., J. Chem. Phys. **152**, 020901 (2020)*

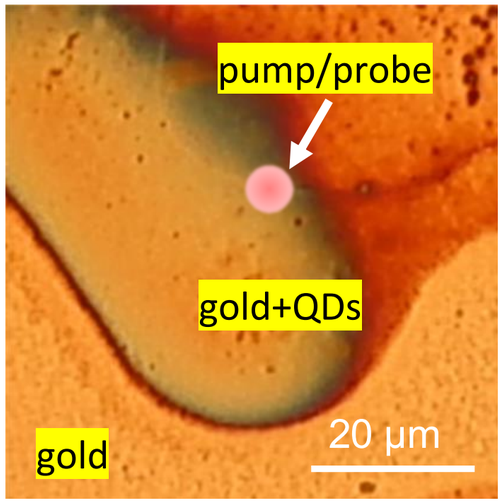
Transient absorption curve, example



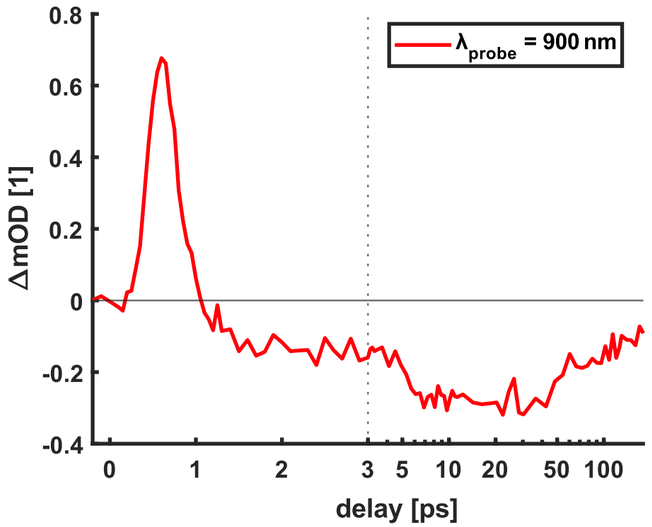
pump-probe set up, Pascal Heim

pump: λ (energy) = 650 nm (1.91 eV)
probe: λ (energy) = 900 nm (1.38 eV)

$$\mathbf{\Delta OD(t\_delay)} = log_{10}(\frac{I_{pump,probe}}{I_{probe\ only}})$$



Light Microscope image (reflection)



Transient Absorption Contrasts

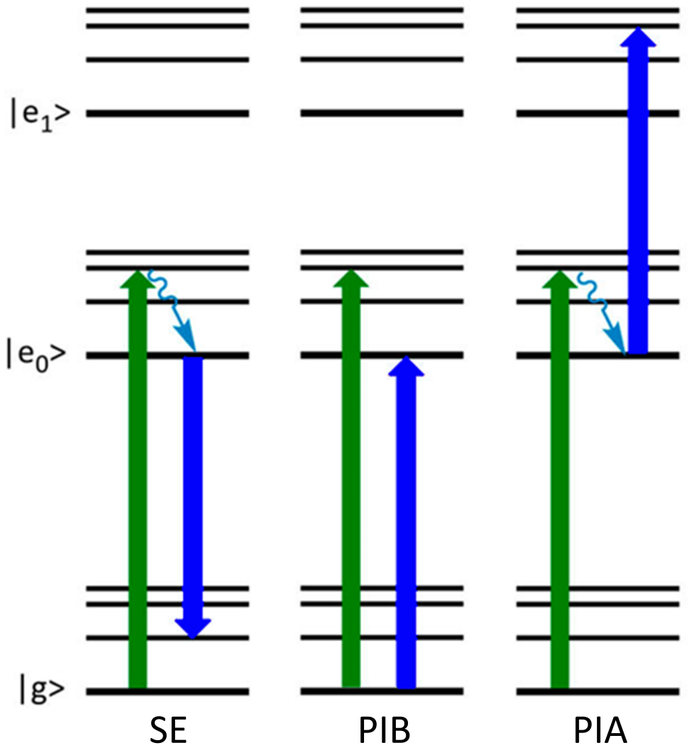
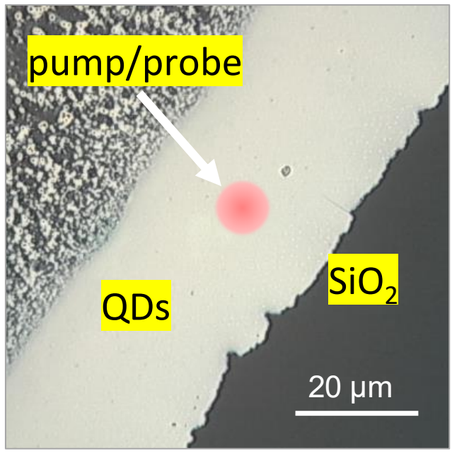


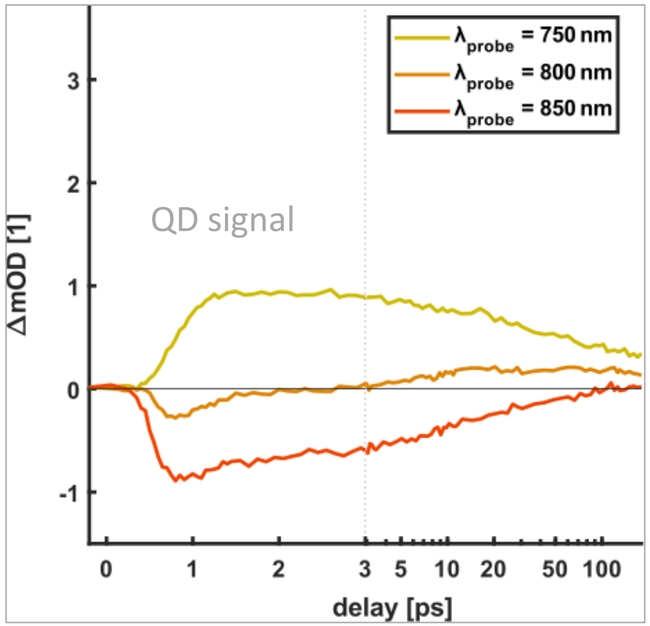
***Image adapted from**: Y. Zhu et al., J. Chem. Phys. **152**, 020901 (2020)*

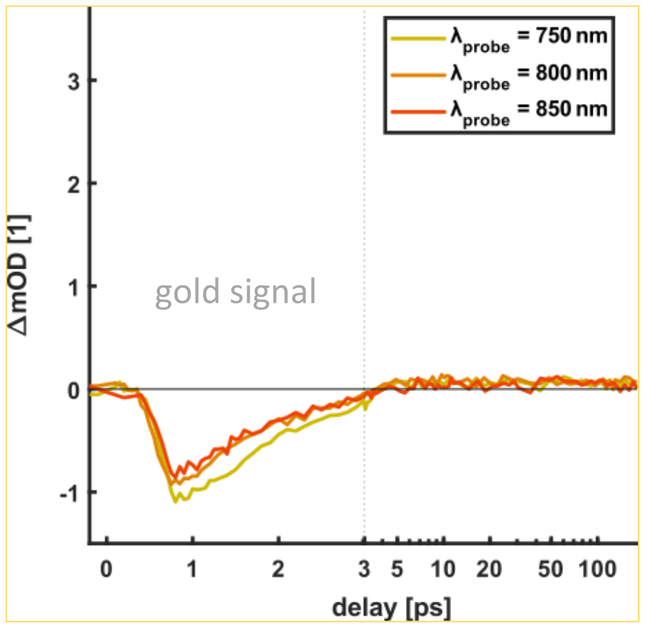
Dario Grimaldi, dario.grimaldi@uni-graz.at

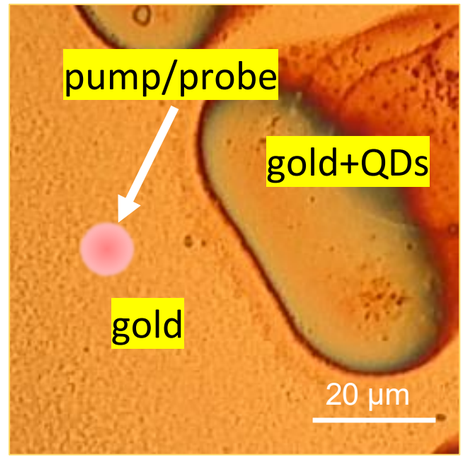
Pure QD film resp. pure gold film: transient absorption



Light Microscope image (reflection),
QD film thickness = 30 nm







Light Microscope image (reflection)

$$\Delta\mathrm{OD}(\mathrm{t\_delay}) = log_{10}(\frac{I_{pump,probe}}{I_{probe\ only}})$$

PIB & PIA:

- photoinduced bleach for (sub-)bandgap probe energies -> ΔmOD ↓
- photoinduced absorption for above-bandgap probe energies -> ΔmOD ↑

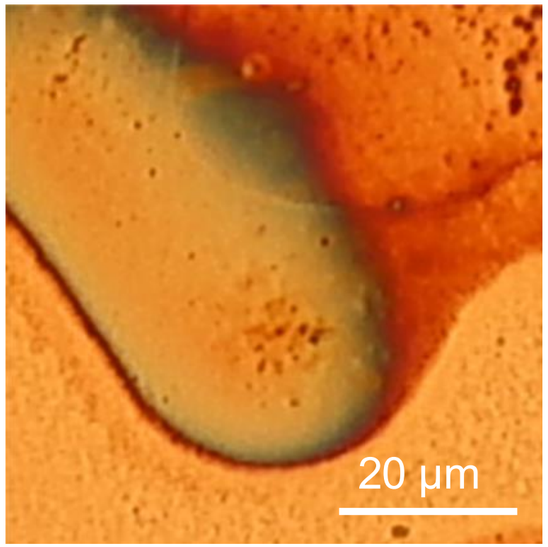
EEI & EPI:

- e^- distribution is thermalized after EEI (EEI, e^- - e^- interactions, **fs** scale)
- thermalizes further with cold lattice (EPI, e^- - ph interaction, **ps** scale)

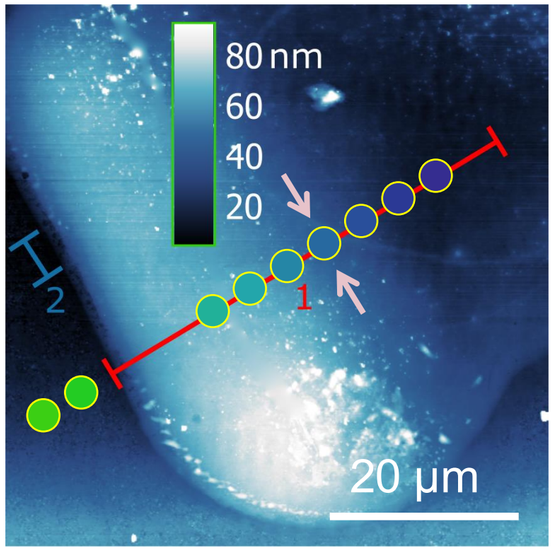
*T. Ghosh et al., ACS Nano, **12,** 5719–5725 (2018)*

*G. Della Valle et al., Phys. Rev. B **86**, 155139 (2012)*

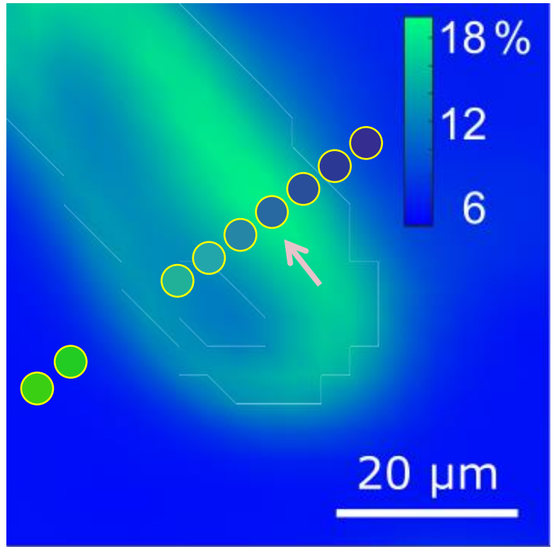
Hybrid system: enhanced transmission



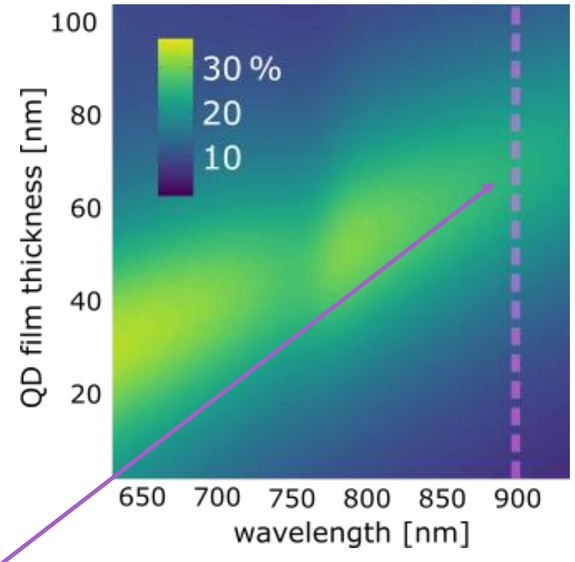
Light Microscope image (reflection)



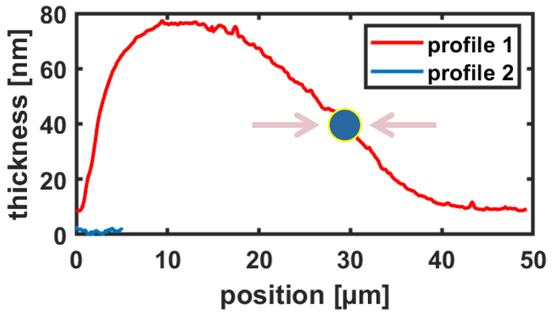
Atomic Force Microscopy image

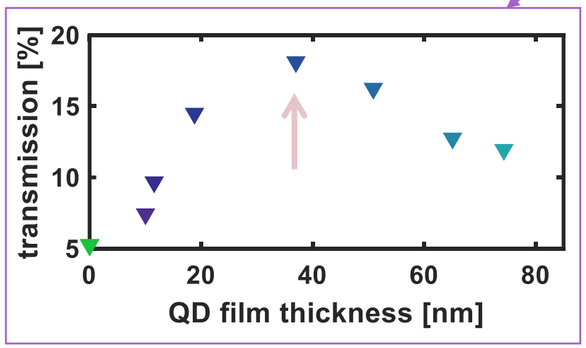


Transmission image, **λ = 900 nm**



Calculated transmission for a QD film on top a 30 nm gold film

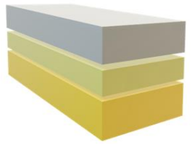


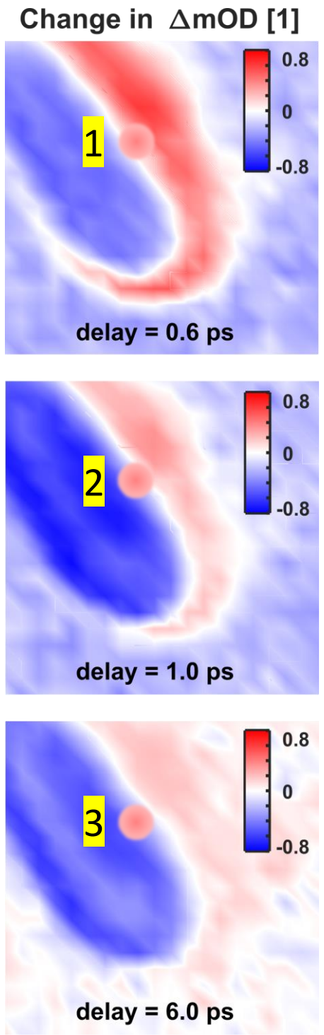


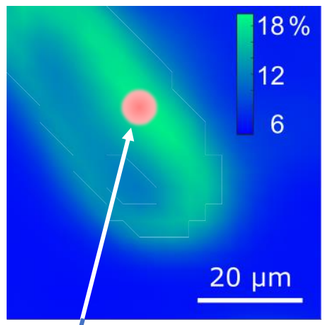
-> strong interference observed for a QD film thickness of 35-40 nm

Dario Grimaldi, dario.grimaldi@uni-graz.at

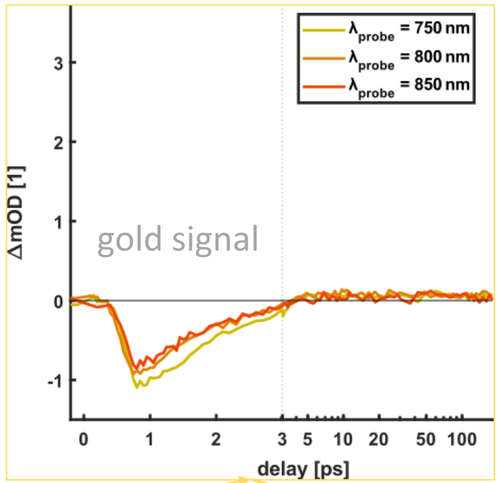
Hybrid system: transient absorption

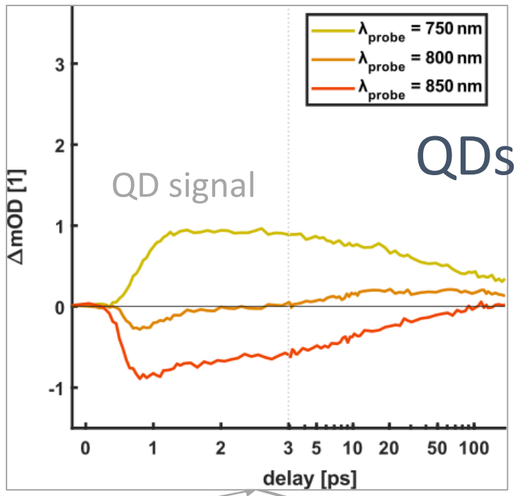




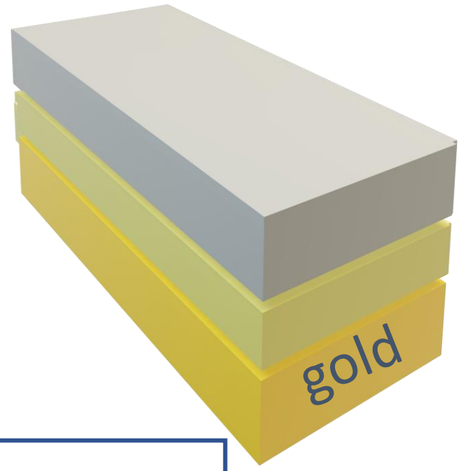


pump/
probe





QDs {



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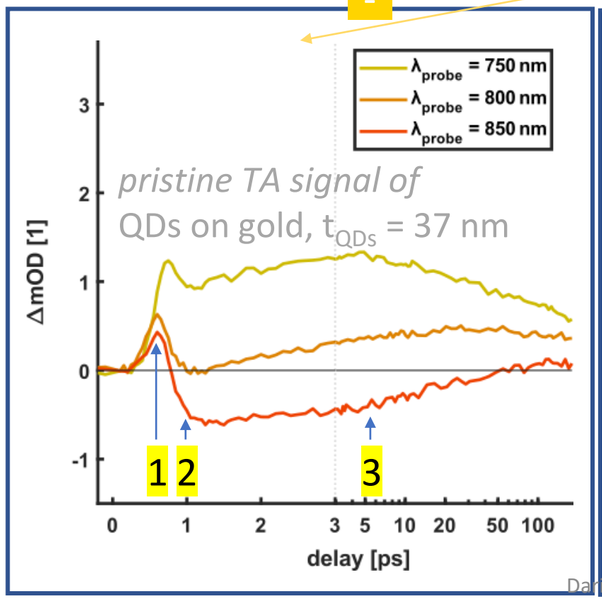
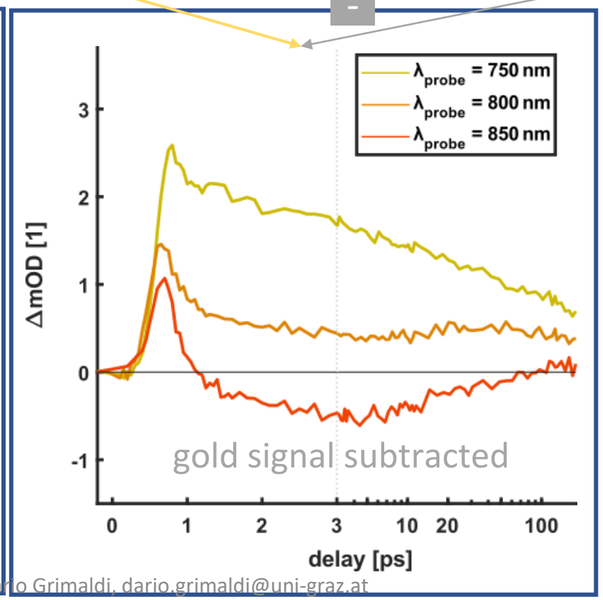
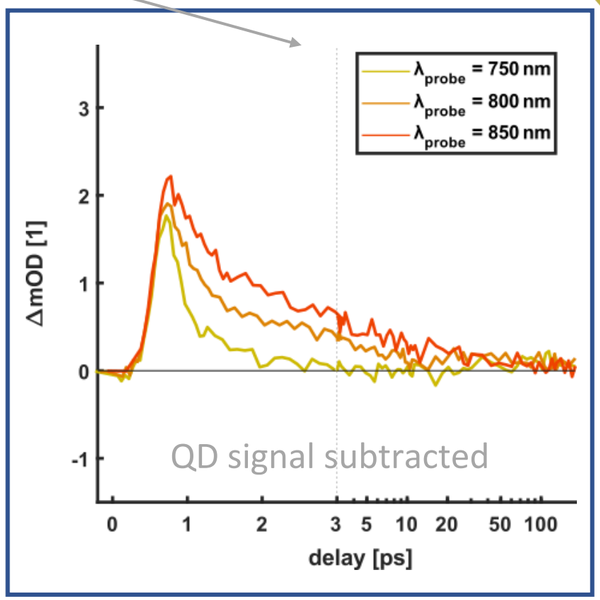


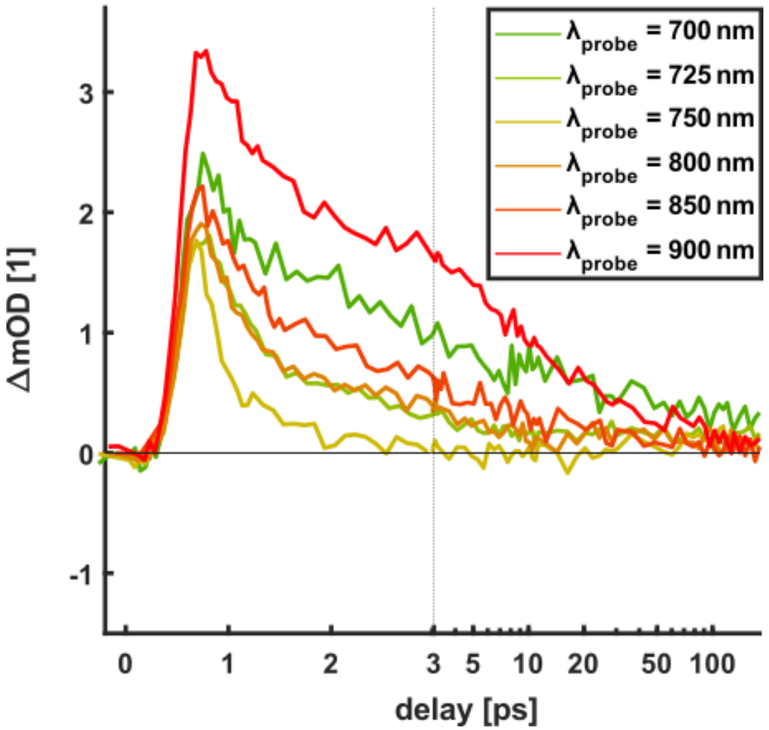




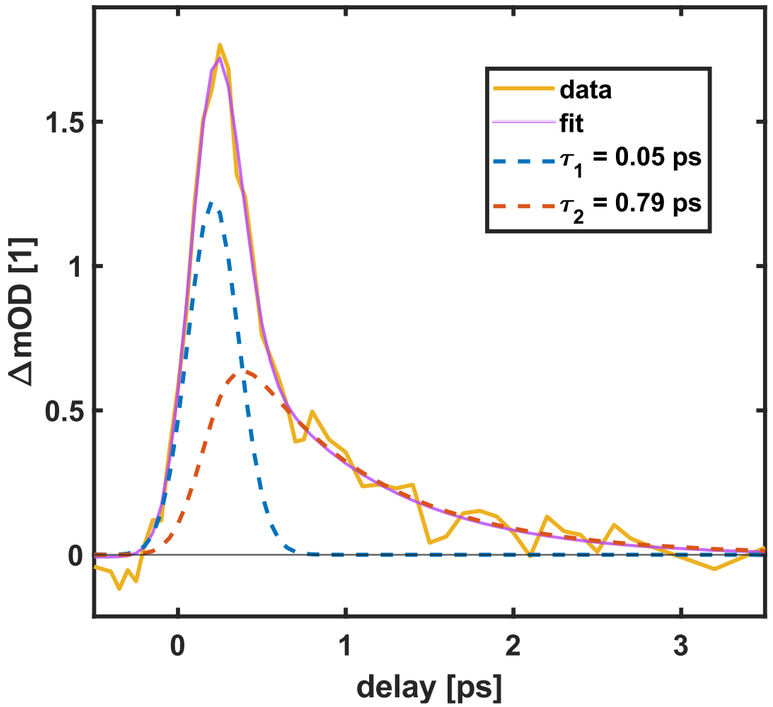
2D maps of TA (cf. λ_{probe} = 850 nm)

Hybrid system: sub-picosecond dynamics

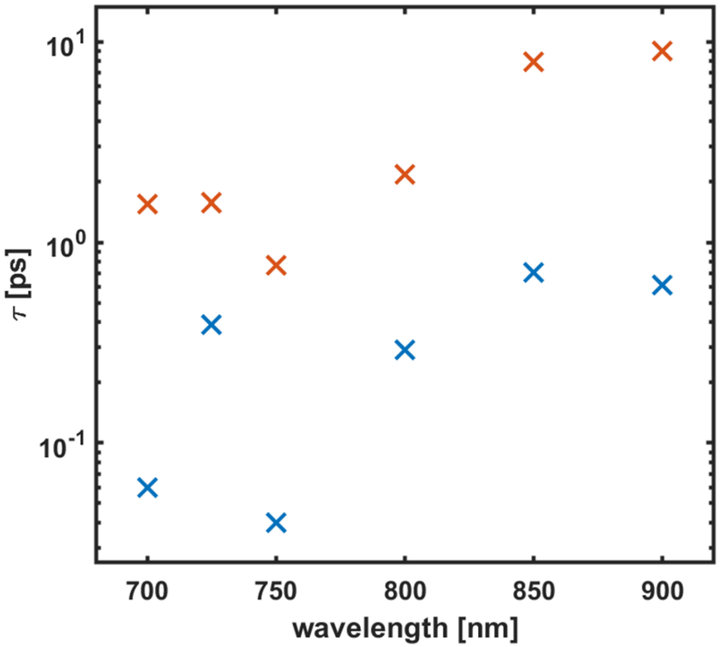
λ_{probe} = 700-900 nm



Exemplary fit for λ_{probe} = 750 nm



Time constants as a function of the probe wavelength
-> minimum at 750 nm



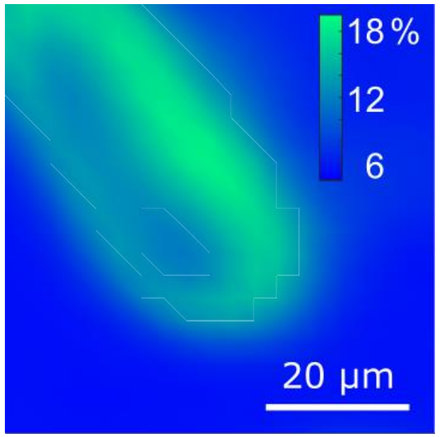
Summary

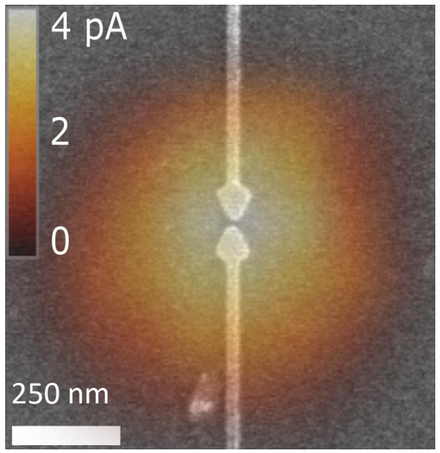
Transient absorption at the hybrid system

- **enhanced transmittance due to strong interference**
- **sub-picosecond dynamics**

Photoconductivity at nanogaps

- **ultrasmall active area**
- **I-F power law dependence**





Outlook

- **Find a theoretical model for the observed ultrafast dynamics**

Acknowledgements

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