Photoconductivity in Gold Nanogaps

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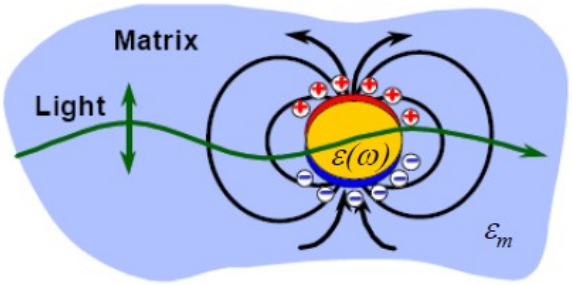
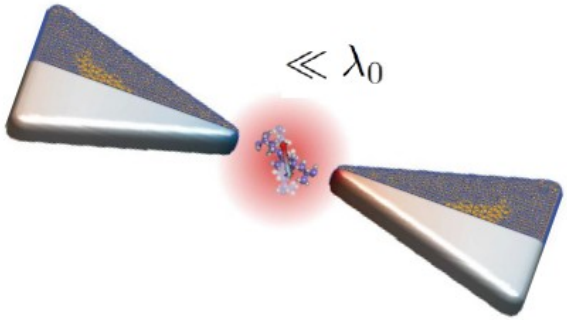
Nano-Optics Research in Graz

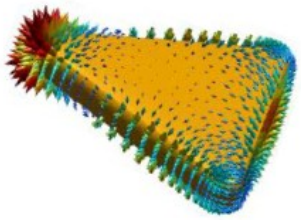


Localized Surface Plasmon Resonance

- enhanced local light fields
  - enhanced excitation
  - local refractive index sensing
  - directed electron emission
- strong and localized absorption
  - local heating with light
- strong scattering
  - enhanced emission
  - cooperative effects in arrays

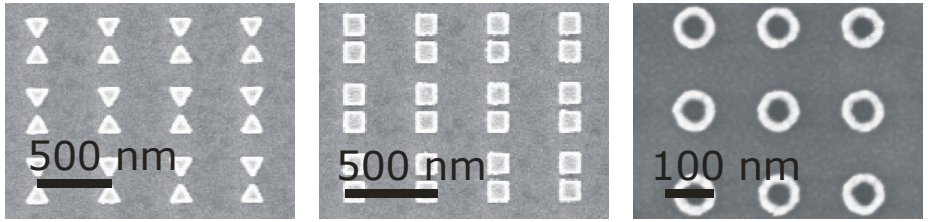


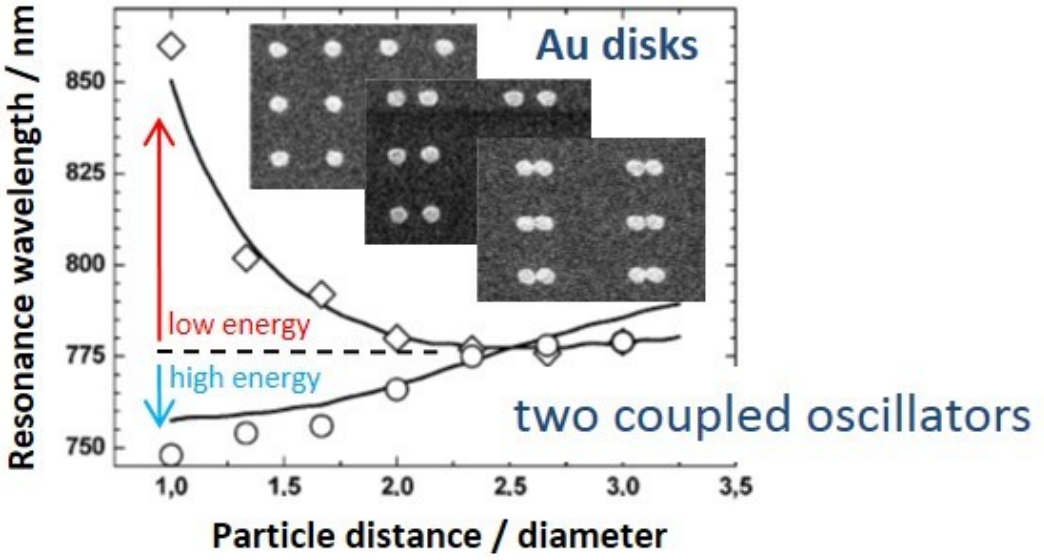
- strongly curved surfaces
- material properties
- surface/volume ratio
- etc.



Electron Beam Lithogarphy

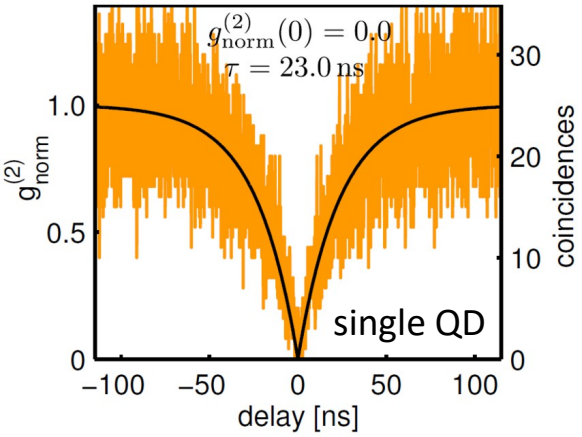
Lithographic tailoring

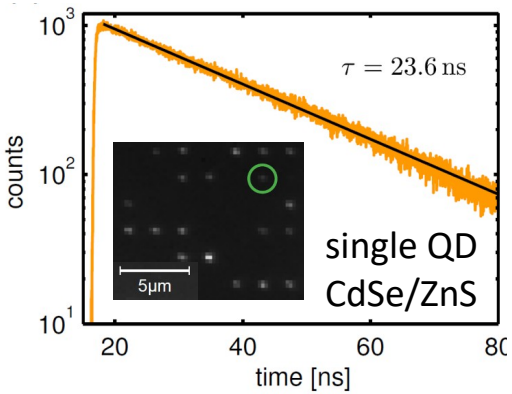


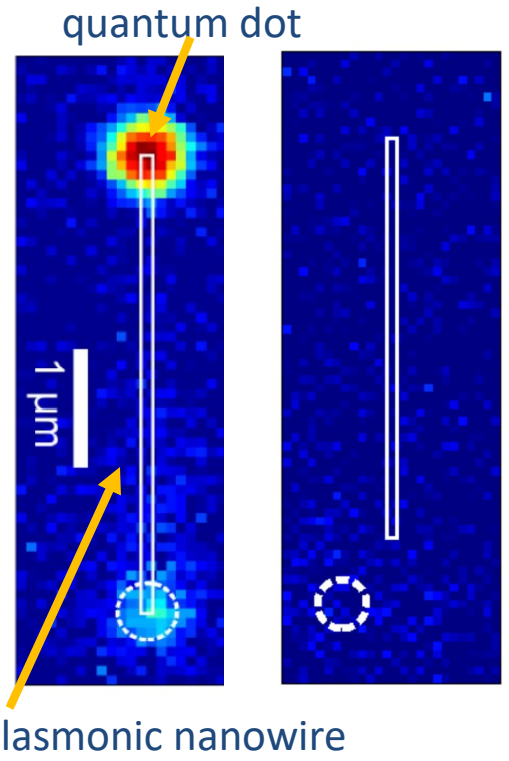


W. Rechberger et al., Opt. Commun. 220, 137 (2003)

Buliding hybrid nanostructures

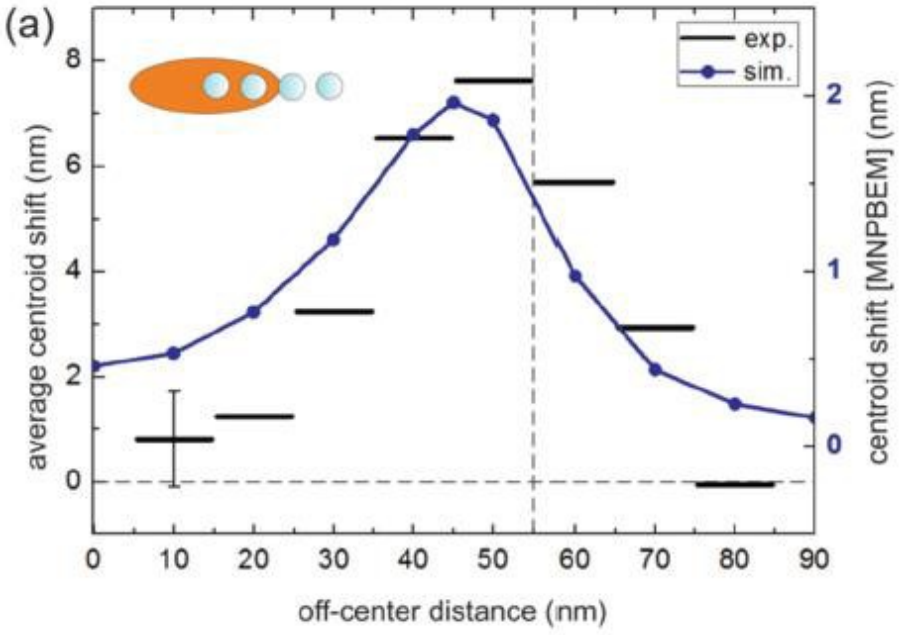


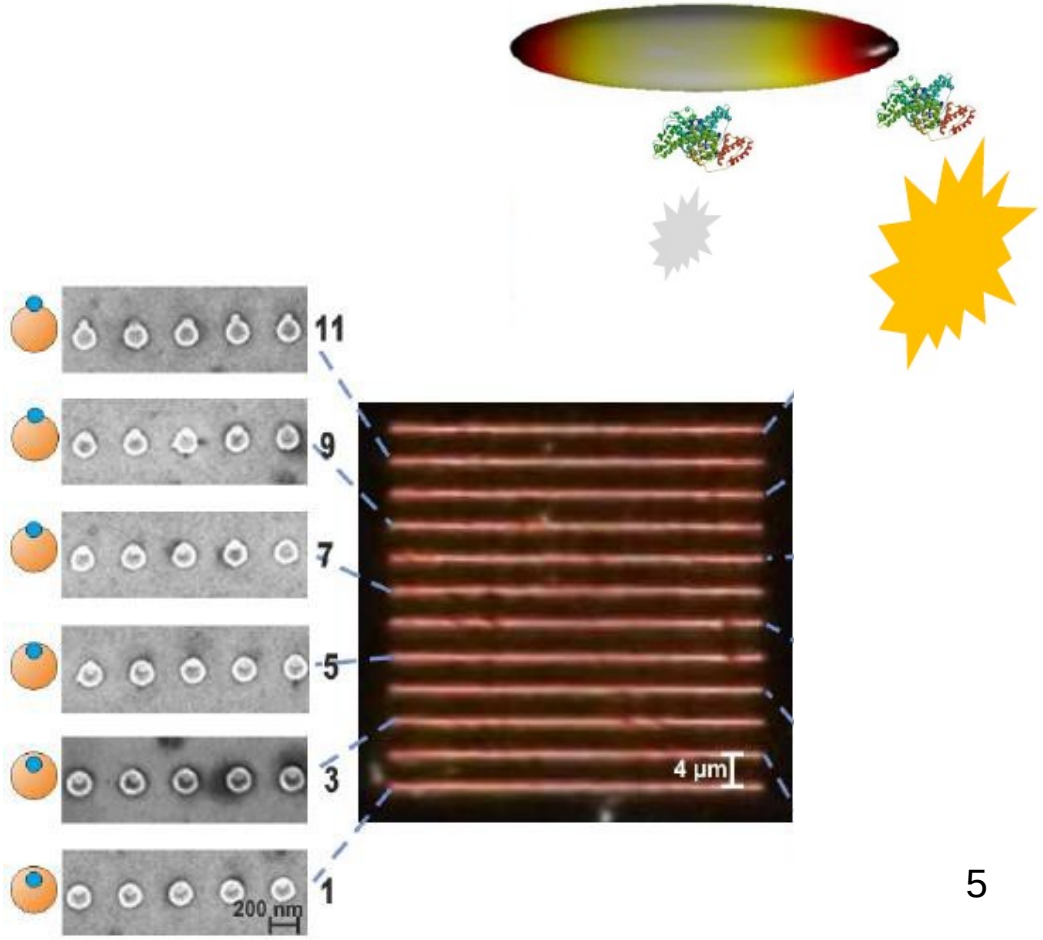




C. Gruber et al., Appl. Phys. Lett. 106, 081101 (2015)

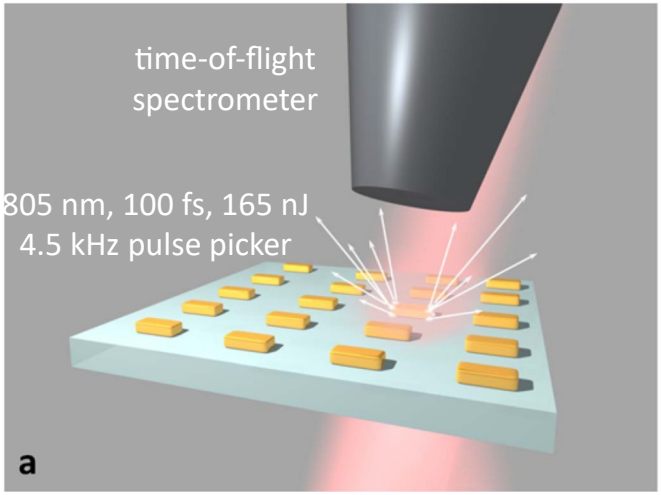
Local Sensitivity to Environment

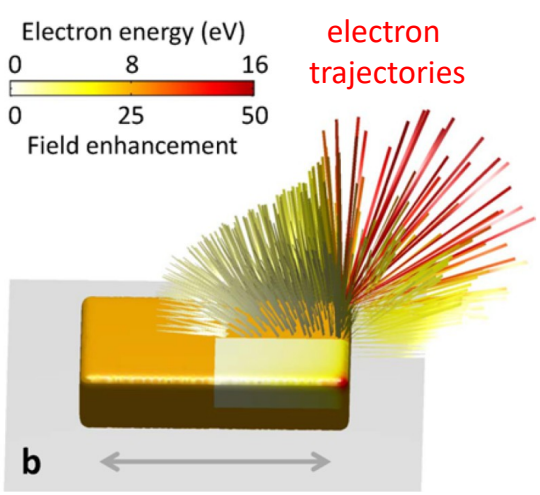


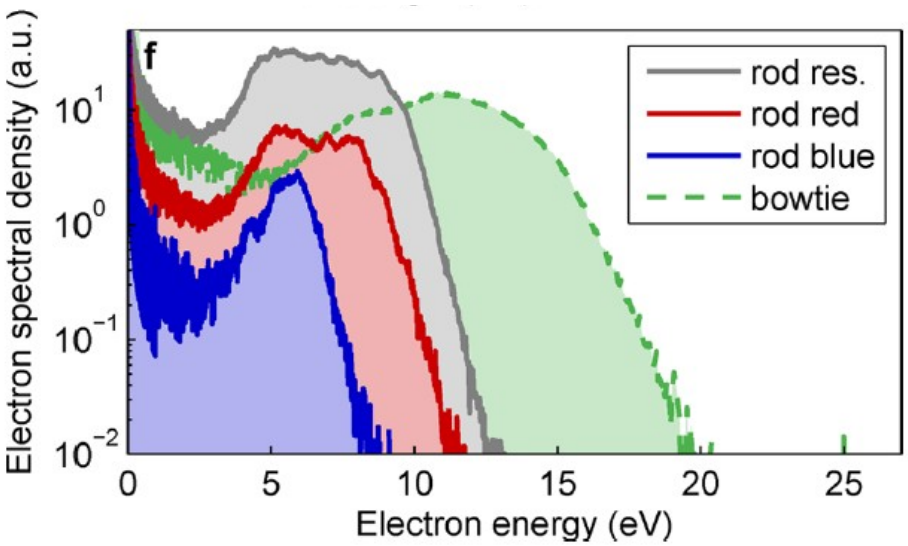


V. Leitgeb et al., Nanoscale 8, 2974 (2016)

High Energy Electron Emission



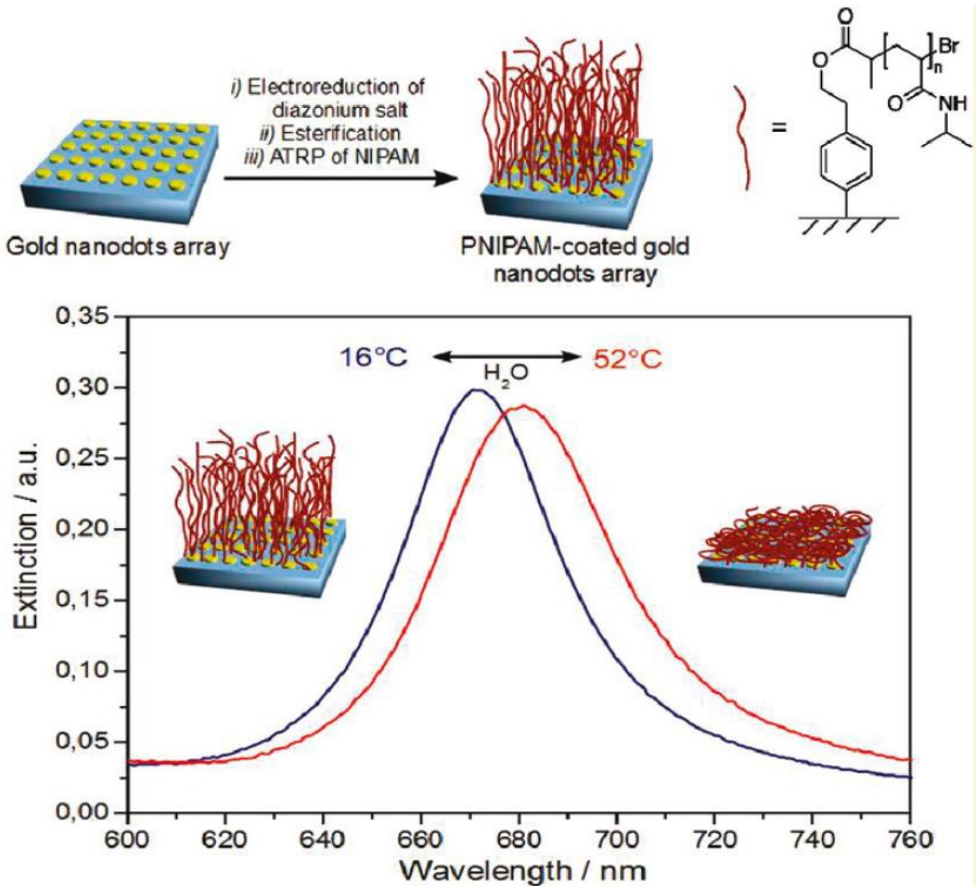




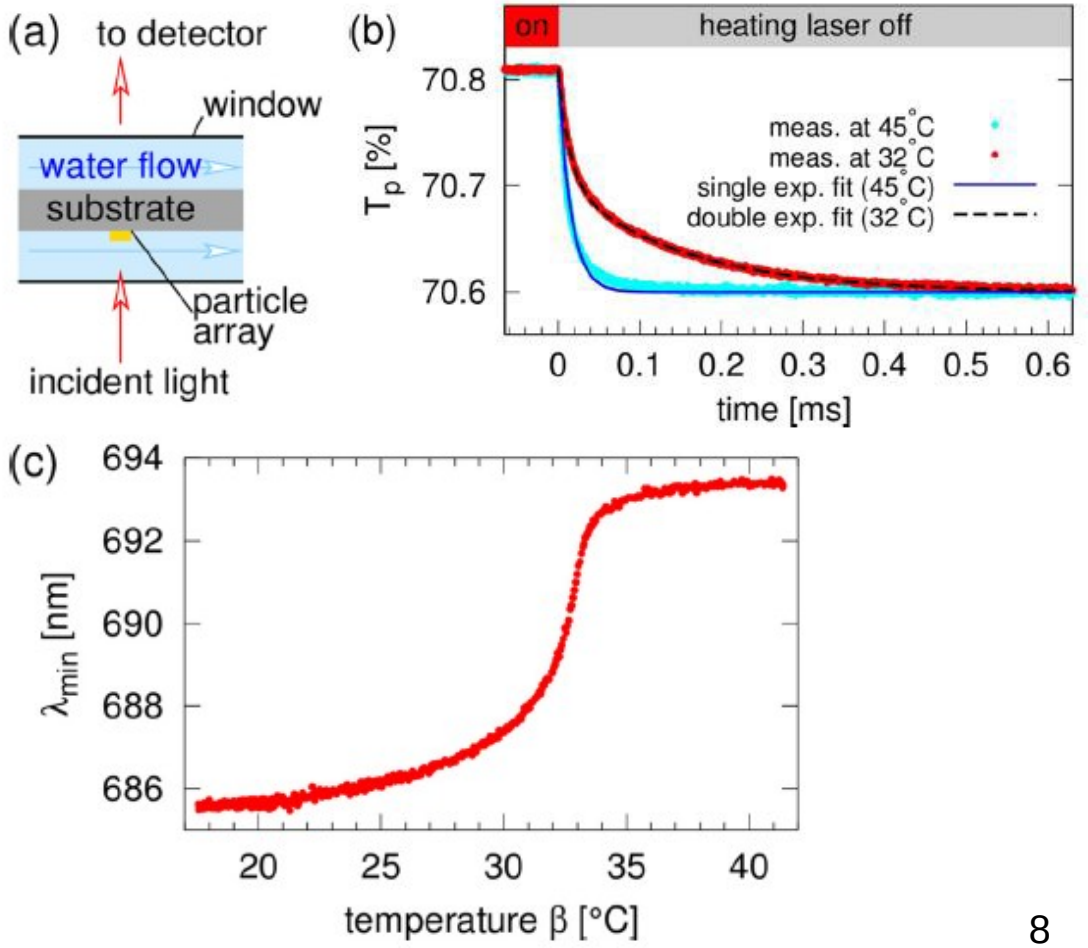
Collaboration with Peter Dombi (Budapest) and Ulrich Hohenester (Graz)

P. Dombi et al., Nano Lett. 13, 674 (2013)
P. Razc et al., Nano Lett. 17, 1181 (2017)

Local Heating Induced Phase Change

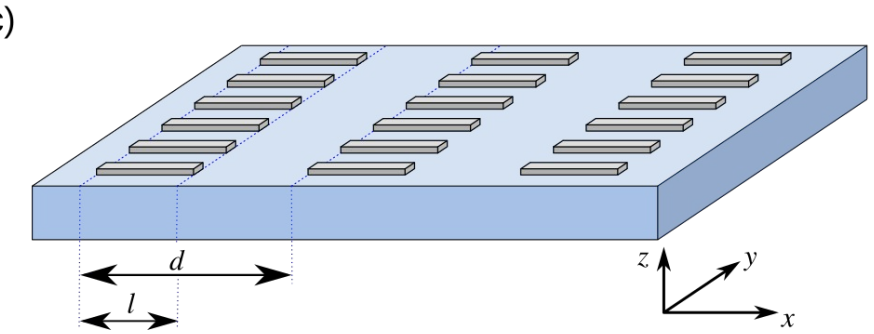


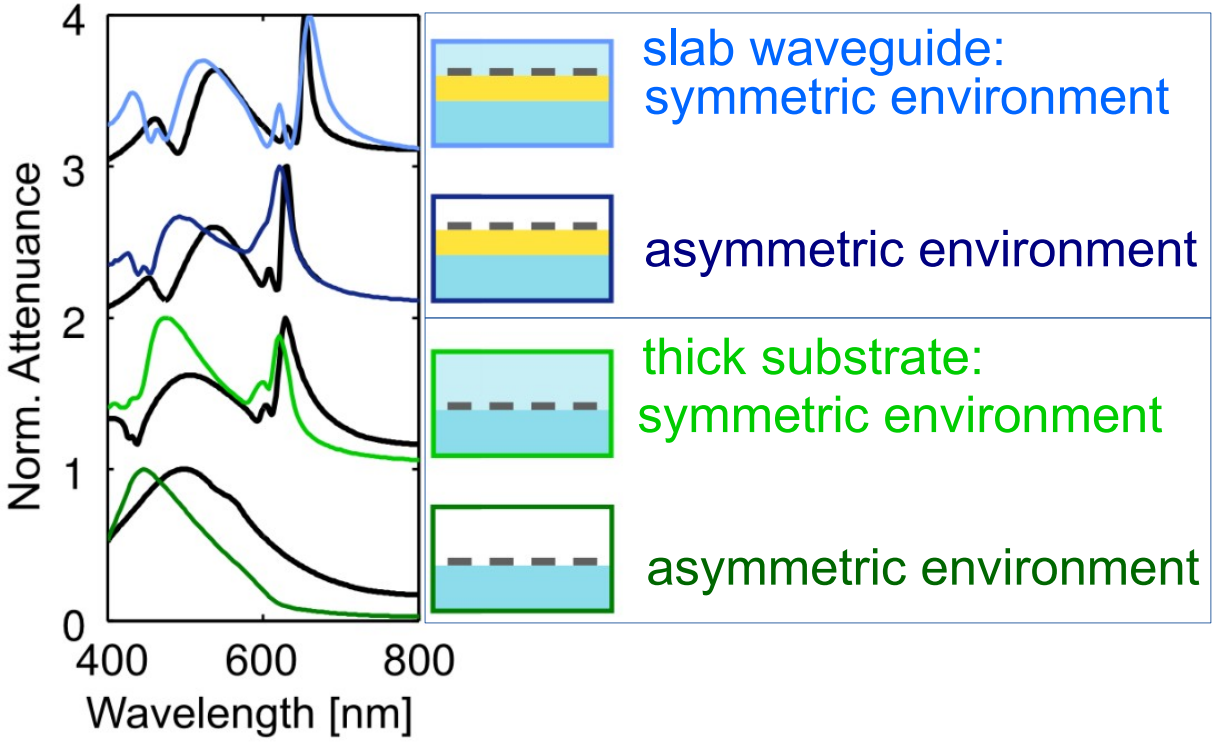
P. Winkler et al., Appl. Phys. Lett. 107, 141906 (2015)



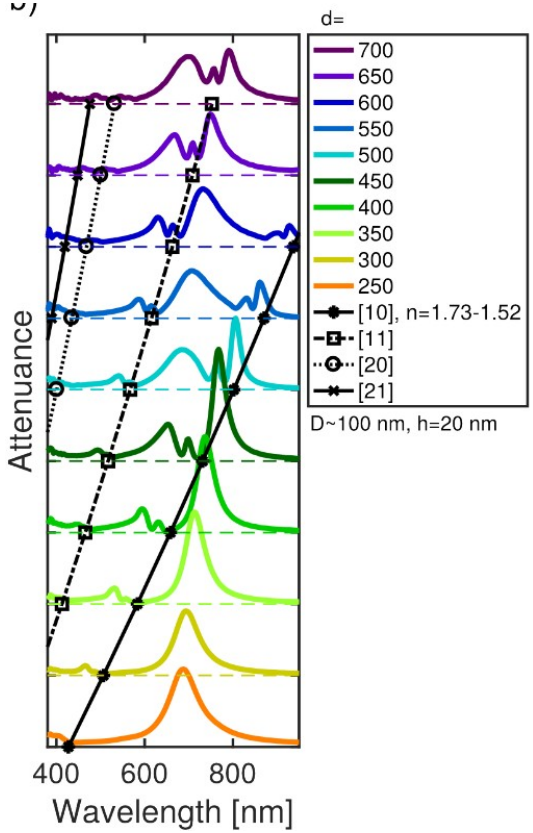
Collaboration with N. Felidj and C. Mangeney

Scattering: Collective Effects

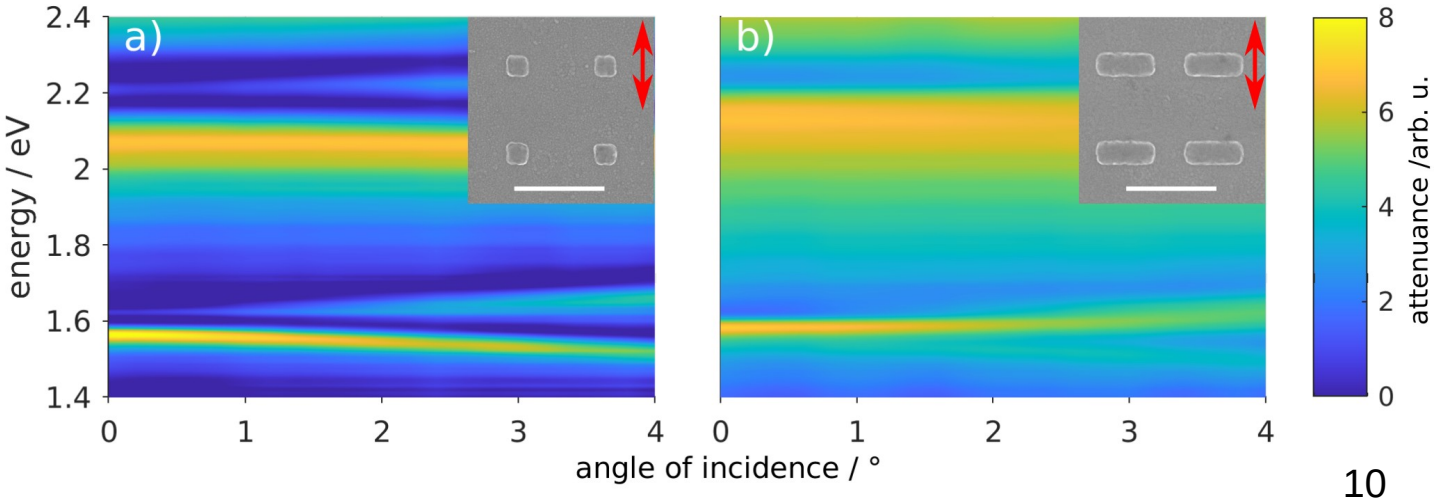




Tunability of Collective Resonances



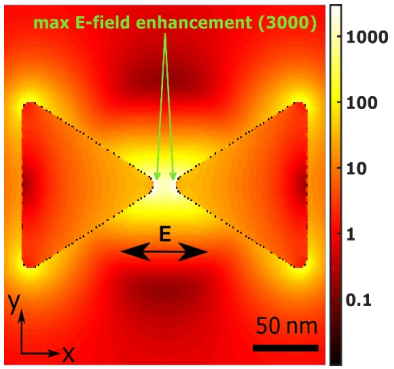
- Narrow and strong attanuance (extinction) peaks promise high field enhancement for surface enhanced spectroscopies
- Peak positions are tunable by array period and angle of incidence



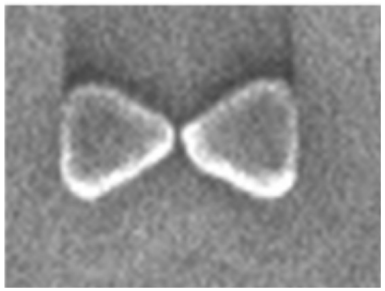
V. Tretnak et al., J. Phys. Chem. C 2020, 124, 3, 2104–2112

Photoconductivity in Gold Nanogaps

Motivation



Simulated optical near field enhancement



Electron micrographs of a gold bow-tie

Bow-tie nanoantennas

- Surface plasmon resonances
- High field enhancement
- Strong coupling to fluorophores in the gap

Can we apply a voltage, for example to build sub-wavelength light detectors?

- Add electric contacts
- Place photo-conductor (quantum dots) in the gap
- Observe plasmonic related effects directly in the photocurrent response

Photoconductivity in Gold Nanogaps

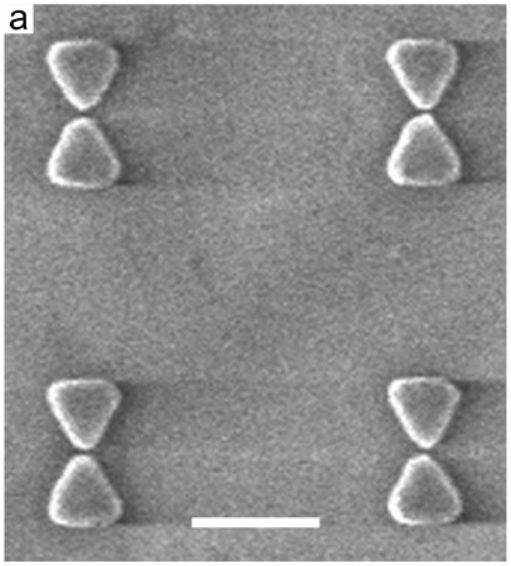
Outline

- Electrode structures and quantum dots
- Photocurrent microscopy
- I-V curves
- Polarization effects
- Photocurrent power-law

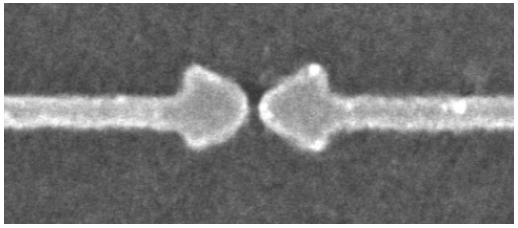
Electrode structures

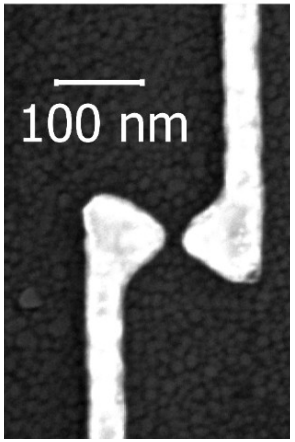
Gold structures on quartz substrate, fabricated by electron beam lithography

Bow-tie structures

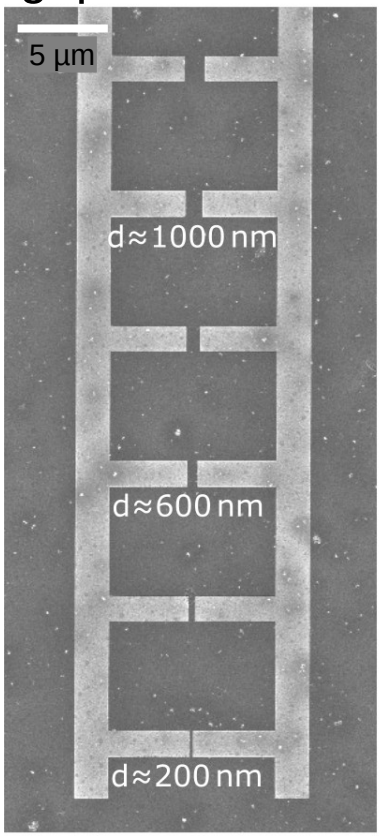


Bow-tie structures with electric connections



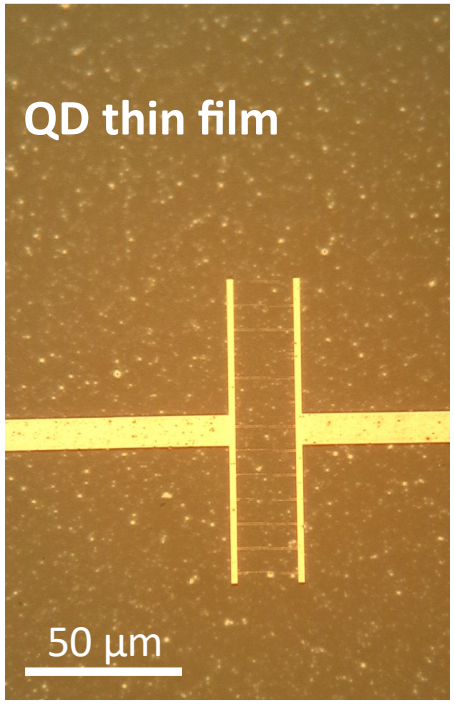


Larger electrode / gap-structures

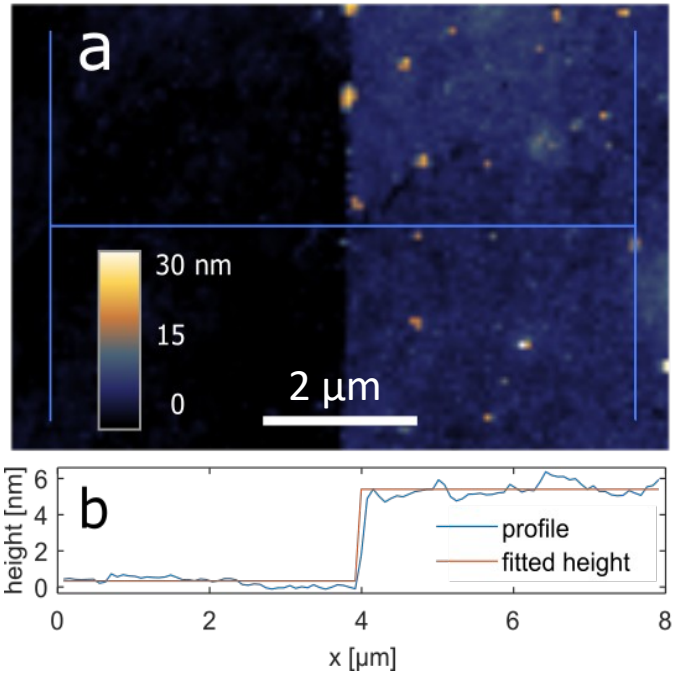


Quantum Dots

PbS-$MAPbI_3$ with ~3.2nm core diameter

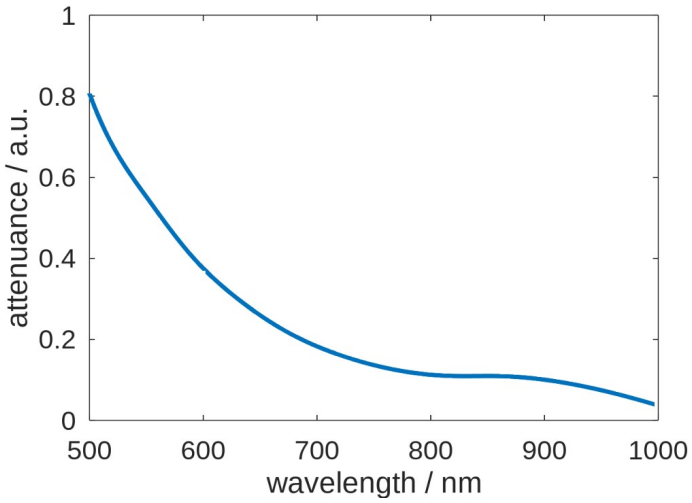


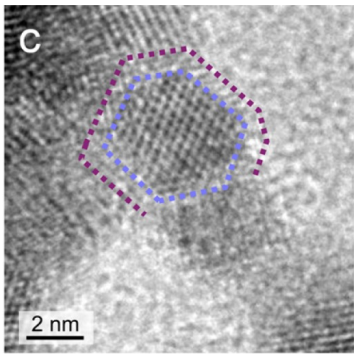
optical microscpe image of sample with QD film



AFM image of QD-film edge

5 nm ≈ 1 monolayer





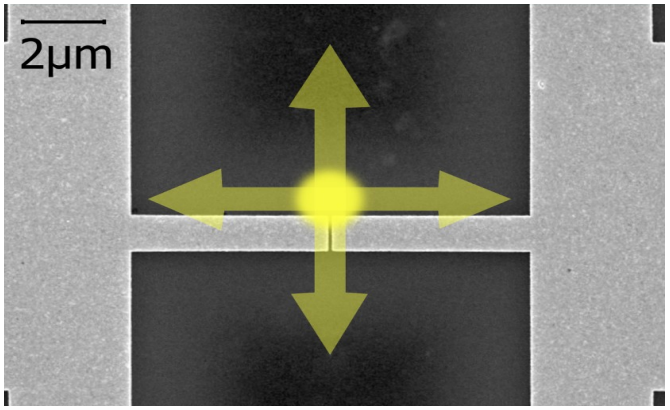
TEM image

D.N. Dirin et al.,J. Am. Chem. Soc. **136**, 6550–6553 (2014).

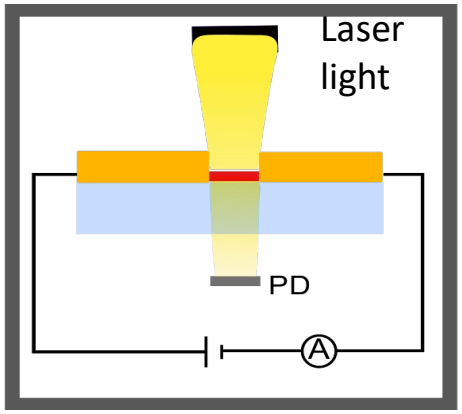
Photocurrent Microscopy

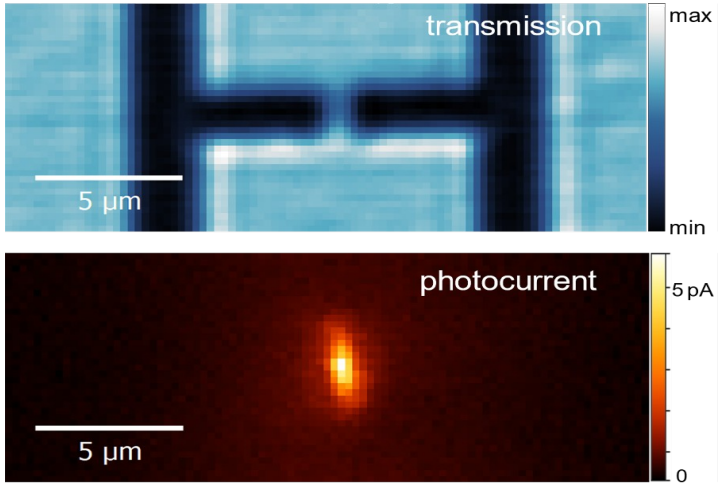
Scanning **P**hoto-**C**urrent **M**icroscopy SPCM

Top view



Side view

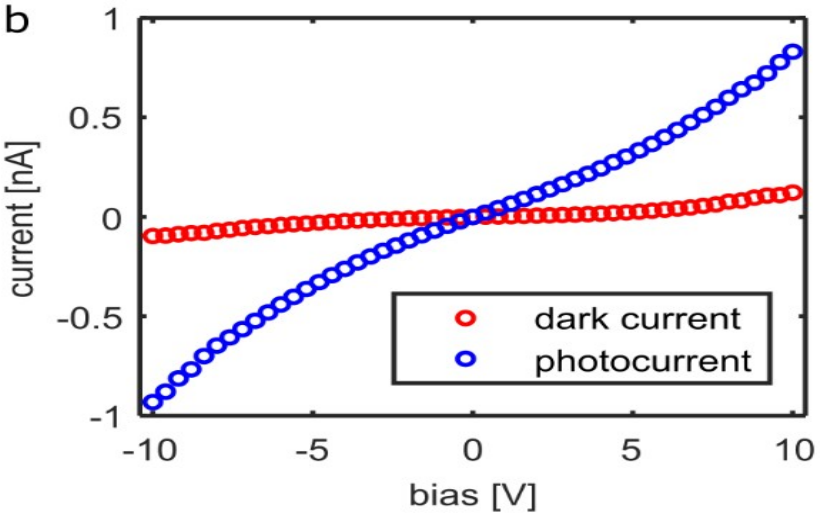




SPCM overlapped to a SEM image

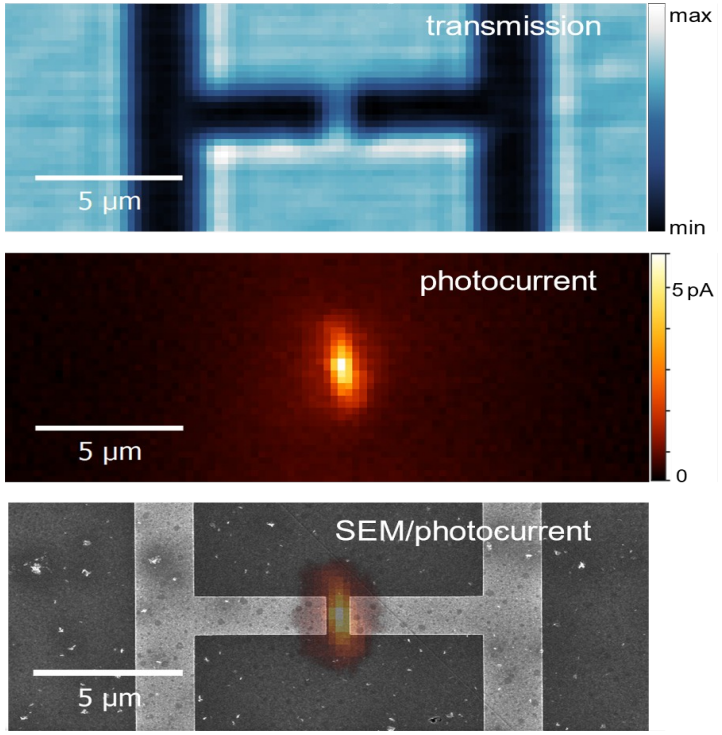
- wavelength-tunable laser, focused (d≈1 µm)
- bias source and ammeter
- piezo scanning stage
- photo-diode to measure transmitted light

I-V-Curves



expectation

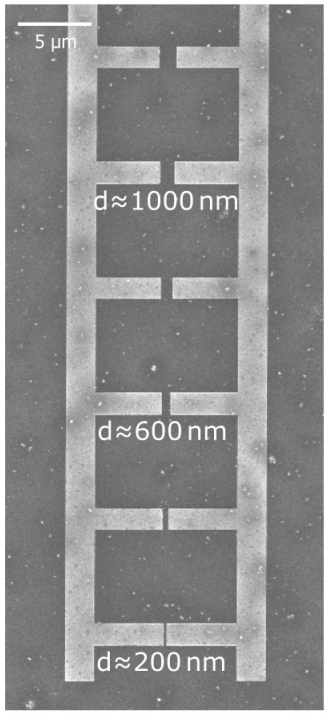
$$I = \frac{U}{R} = \frac{U \sigma A}{d}$$



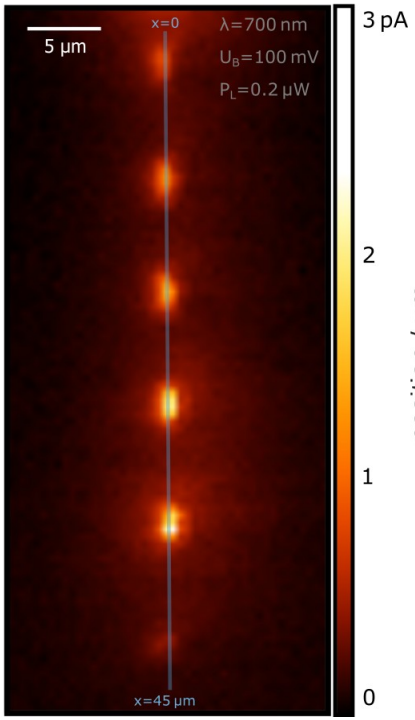
- Nonlinear I-V curves → no ohmic contacts
- Dark current at larger voltages → charge injection from electrodes

Photocurrent Gap-Width Dependence

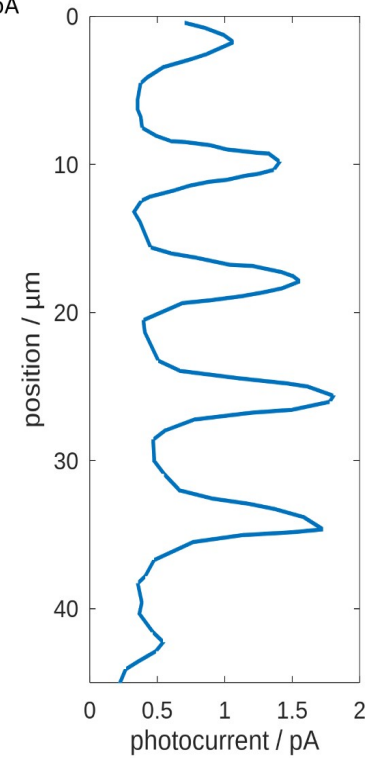
200-1200 nm gap width



SEM



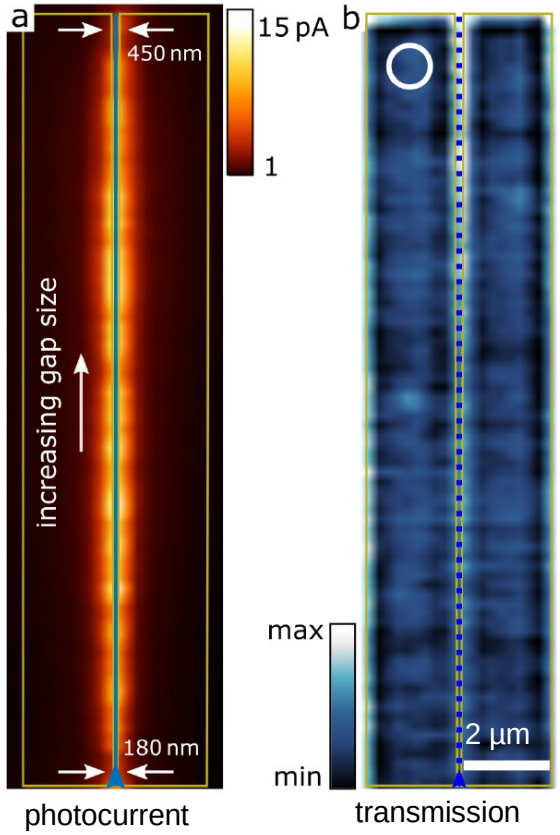
photocurrent



expectation

$$I = \frac{U}{R} = \frac{U \sigma A}{d}$$

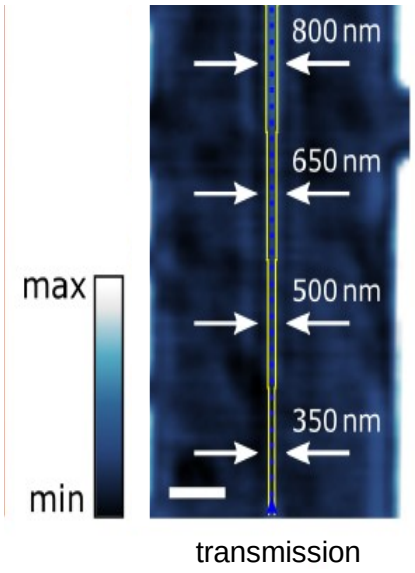
180-450 nm gap width



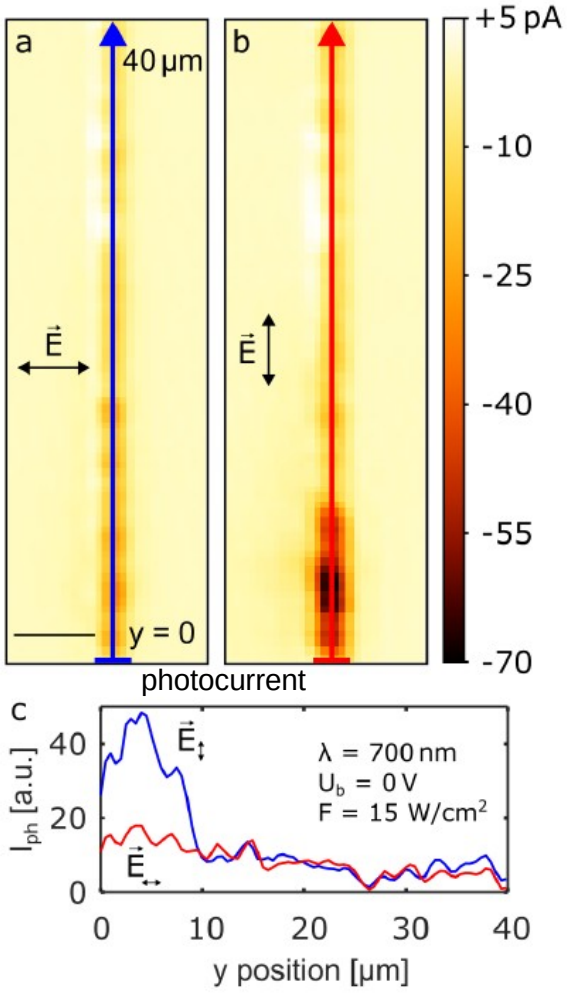
photocurrent transmission

- no homogeneous photoconductor
- exciton quenching by metal bands

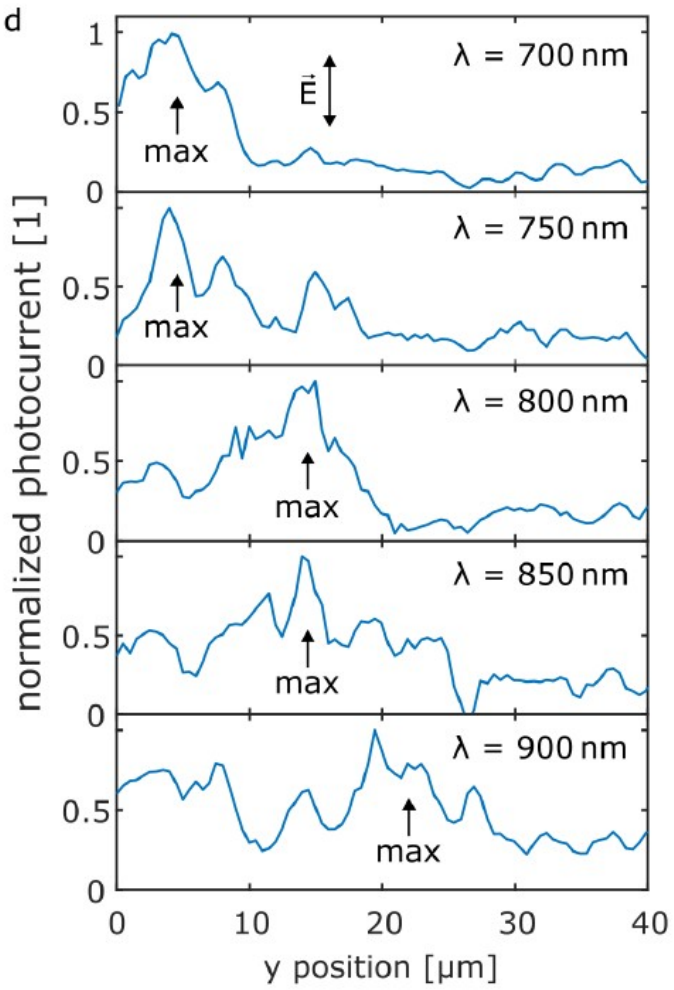
Gap-Width Dependence



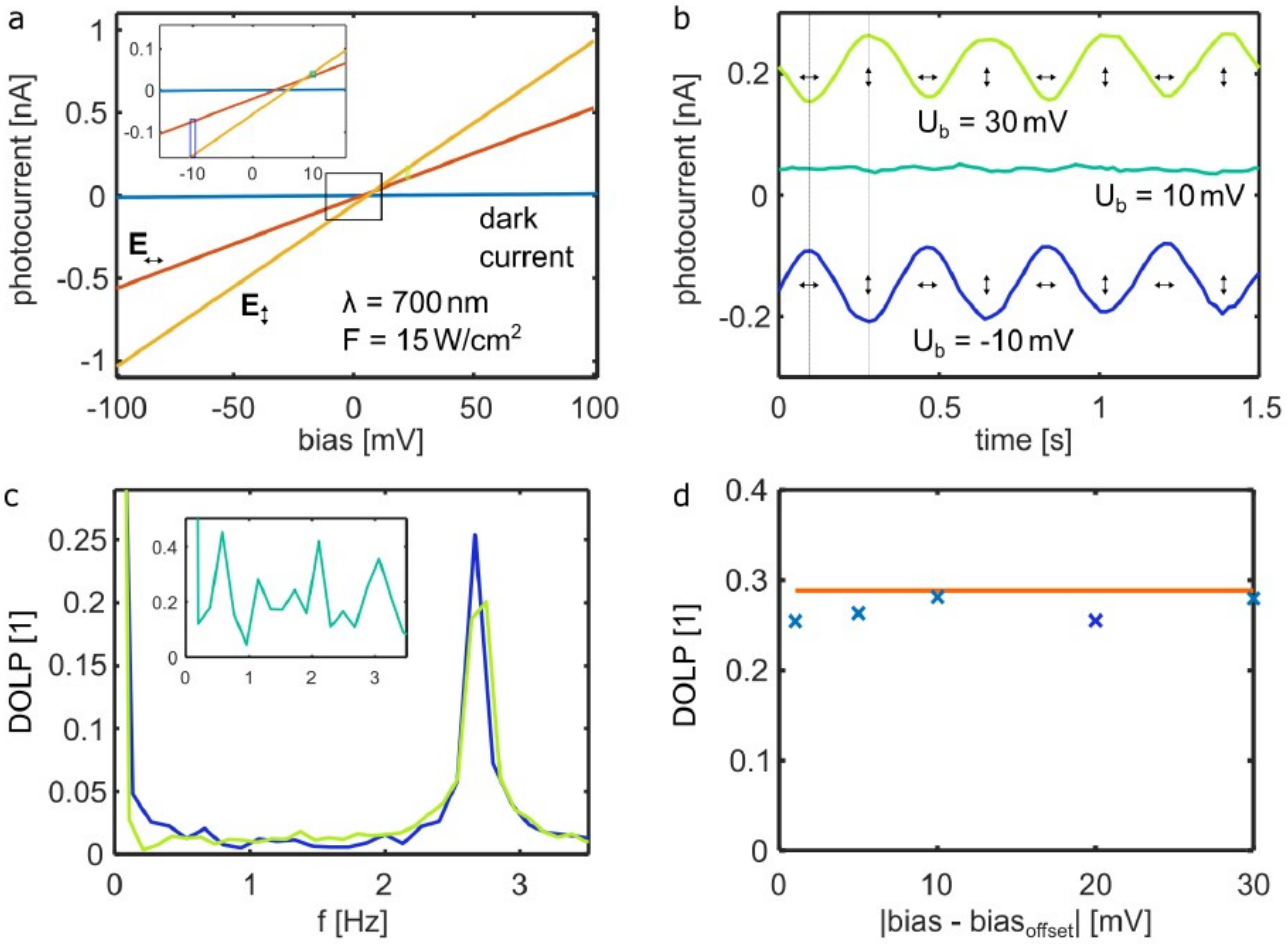
transmission



photocurrent

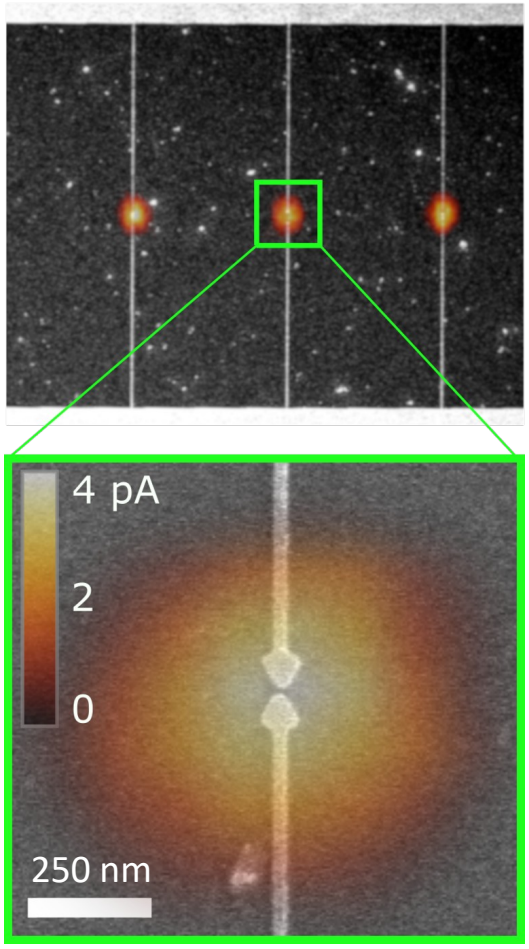


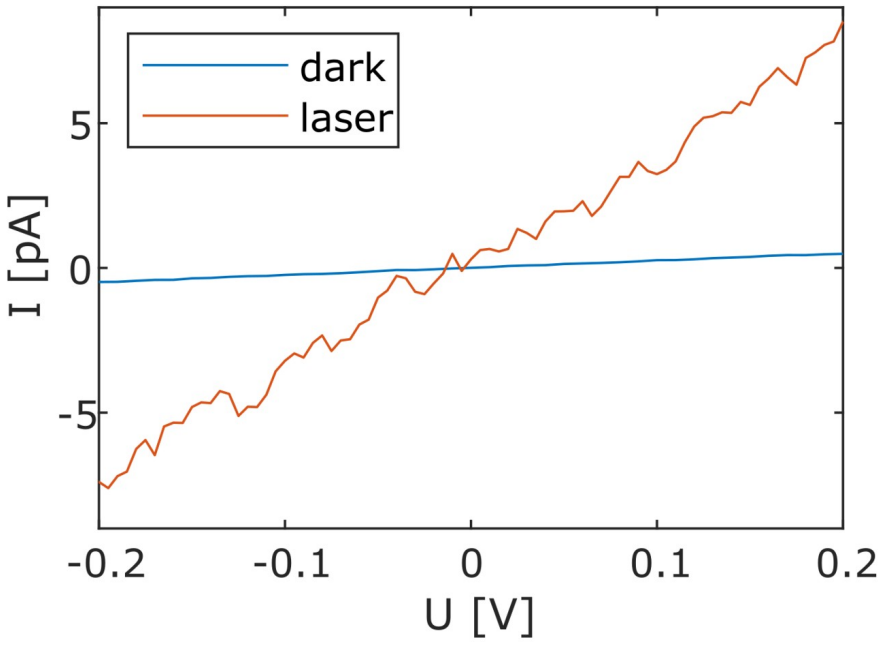
Polarization Effects



- ~30% polarization anisotropy of photocurrent
- larger photocurrent for polarization parallel to electrode edges
- Photocurrent at zero bias

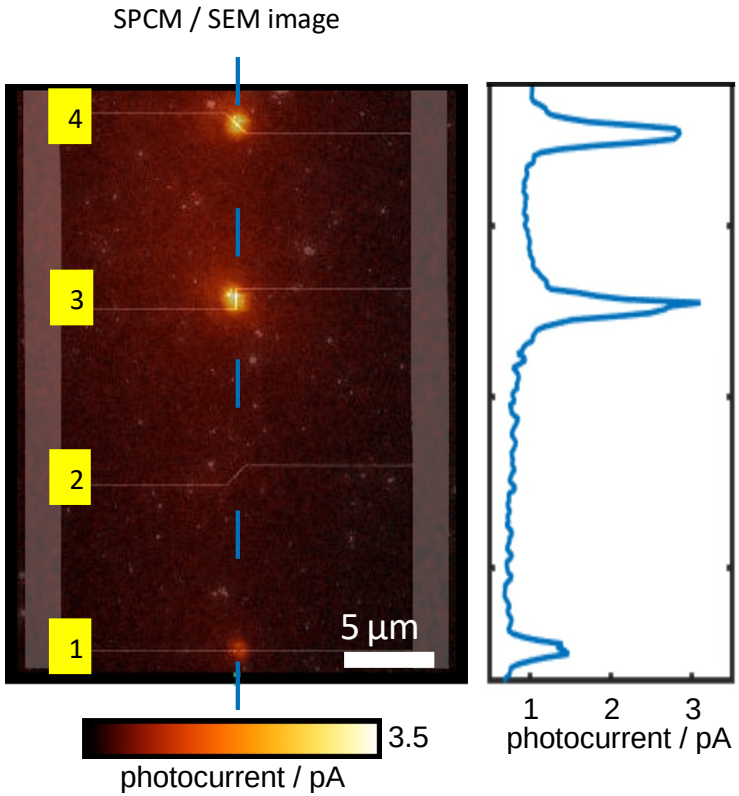
Bow-Tie Structures

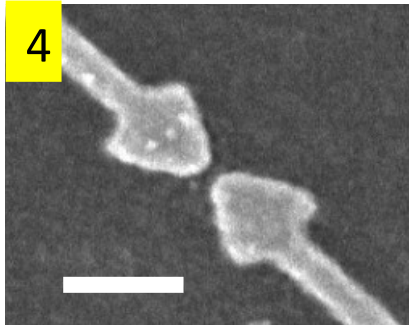


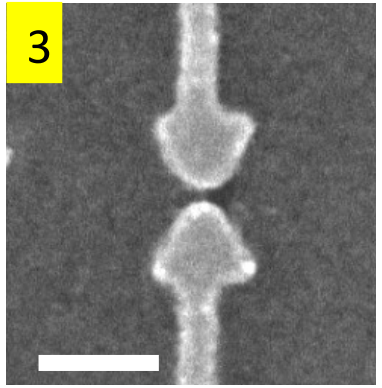


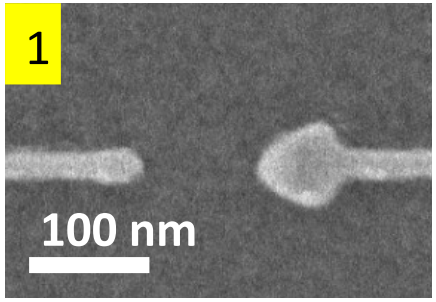
- Reproducible photocurrents from bow-tie structures
- Photocurrent is more noisy than dark-current

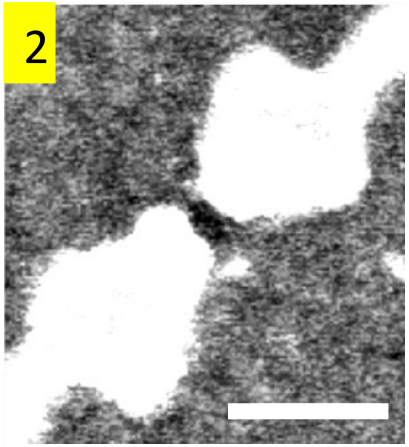
Bow-Tie Structures



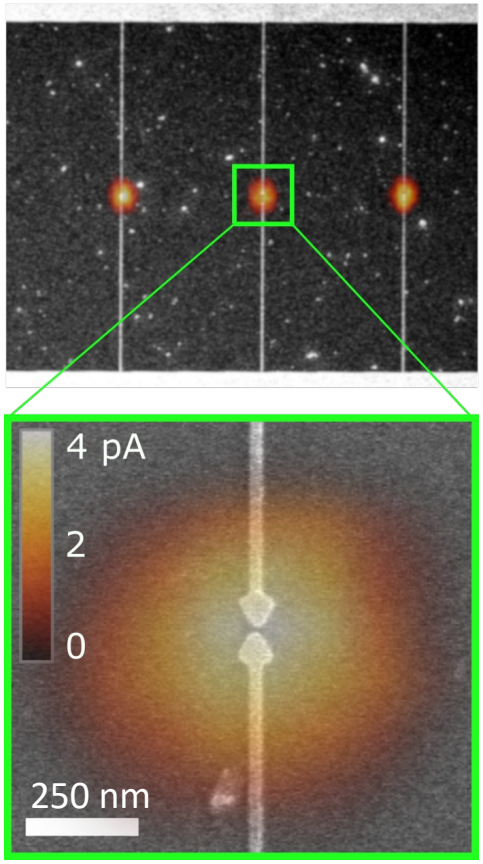


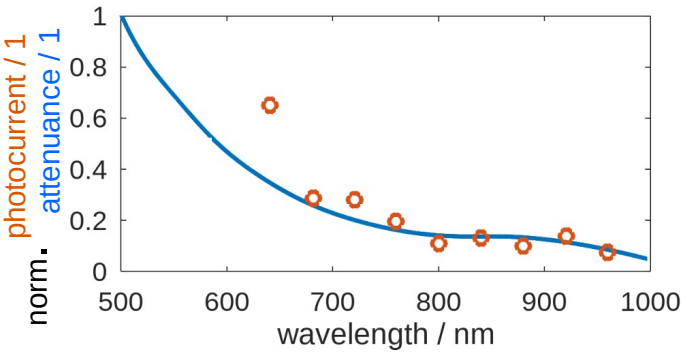


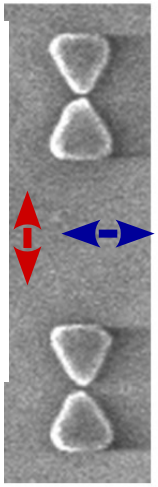


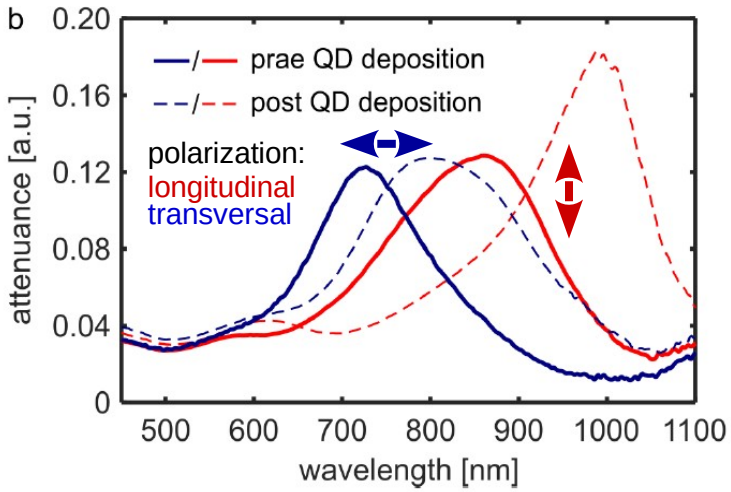


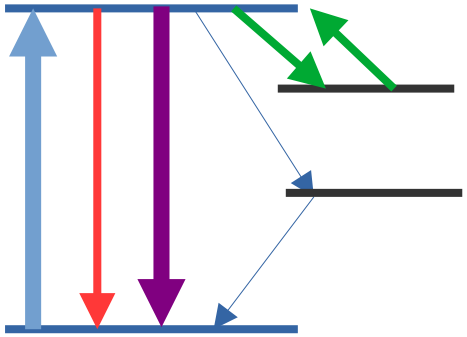
Spectral Response and Polarization Effects in Bow-Tie Structures

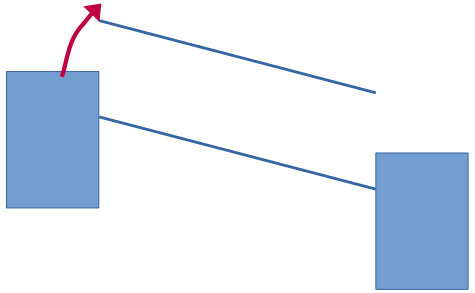








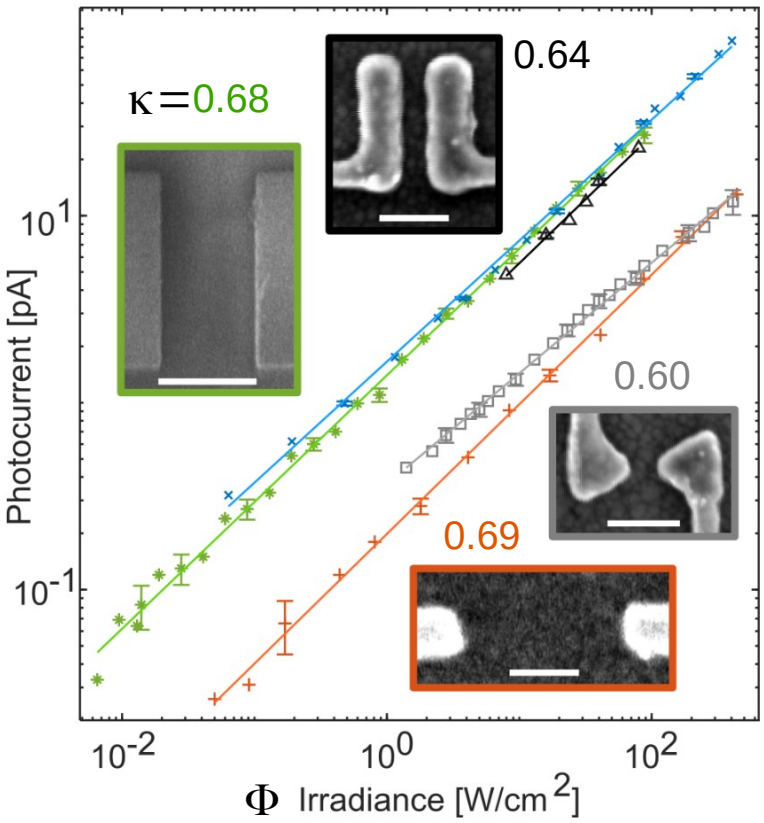




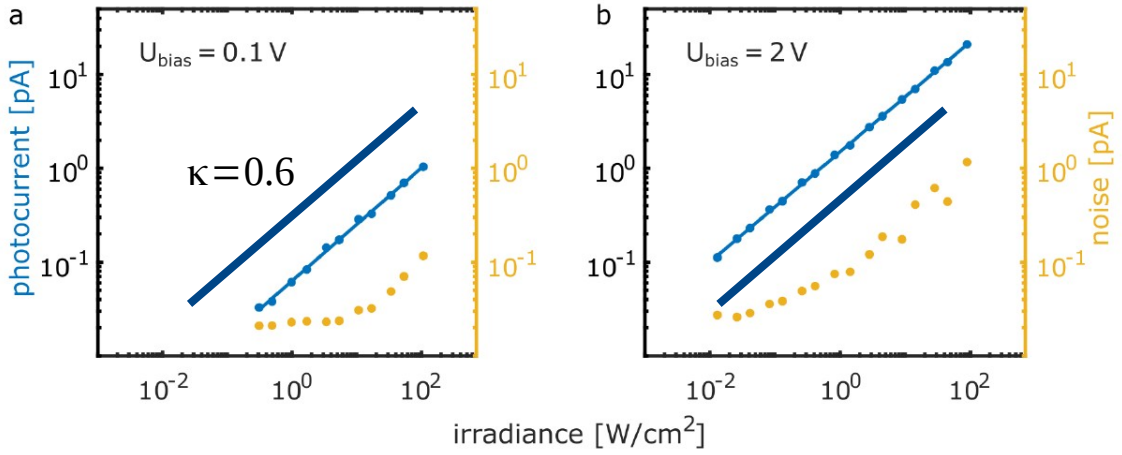
- Polarization anisotropy:~15%; maximum photocurrent for transversal polarization

Photocurrent Power-Law

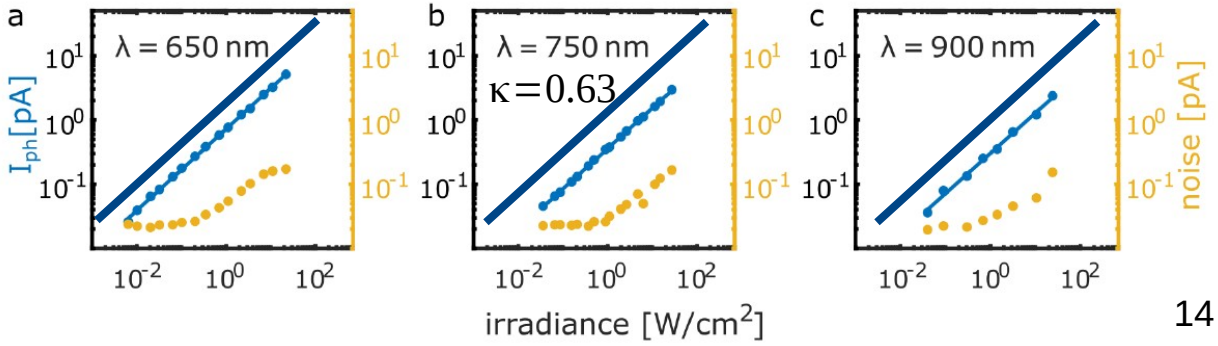
$$I = c \cdot \Phi^{\kappa}$$



bias variation

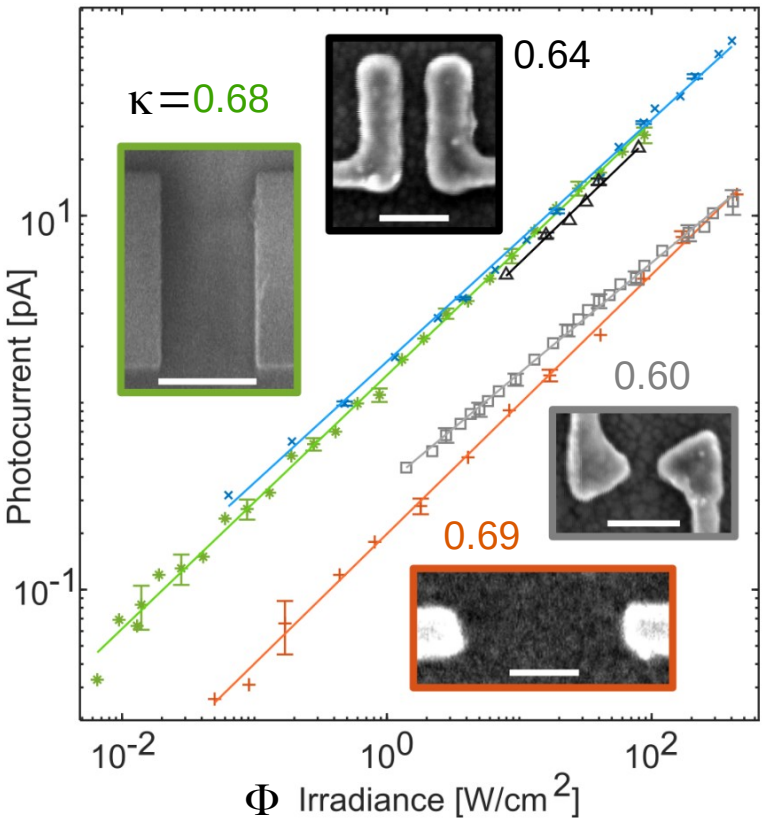


wavelength variation



Photocurrent Power-Law

$$I = c \cdot \Phi^{\kappa} = n \mu q U f_{geom}$$



- Photocurrent follows a power law
- Exponents in the range of κ=0.6-0.7
- Sample-to-sample variations Δκ=0.02
- Some weak influence of electrode geometry

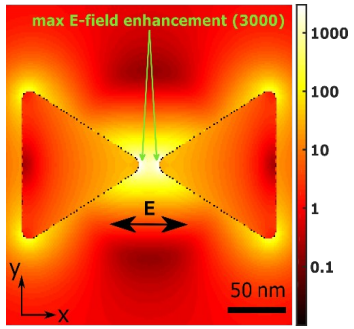
Possible origins of the power law:

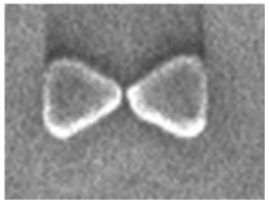
- Trap energy distribution
- Fluctuating percolation paths
- Recombination process dependence on charge carrier density

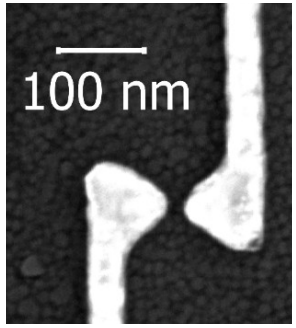
Photoconductivity in Gold Nanogaps

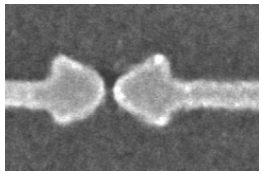
Conclusion

Simulated optical near field enhancement









Electron micrographs of bow-tie structures with and without electric contacts

Bow-tie nanoantennas

- Surface plasmon resonances
- High field enhancement
- Strong coupling to fluorophores in the gap

Can we apply a voltage, for example to build sub-wavelength light detectors?

- Add electric contacts ✅
- Place photoconductor (quantum dots) in the gap ✅
- Observe plasmonic related effects directly in the photocurrent response 🤔 ...not exactly!
- Very stable system - no degradation over month
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See also: D. Grimaldi et al., Nanoscale Adv., 2022, **4**, 3566

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physik.uni-graz.at/en/nanooptics

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- Joachim Krenn






Laboratory of Inorganic Chemistry – ETH Zürich

- Dmitry N. Dirin
- Maksym V. Kovalenko (group leader)


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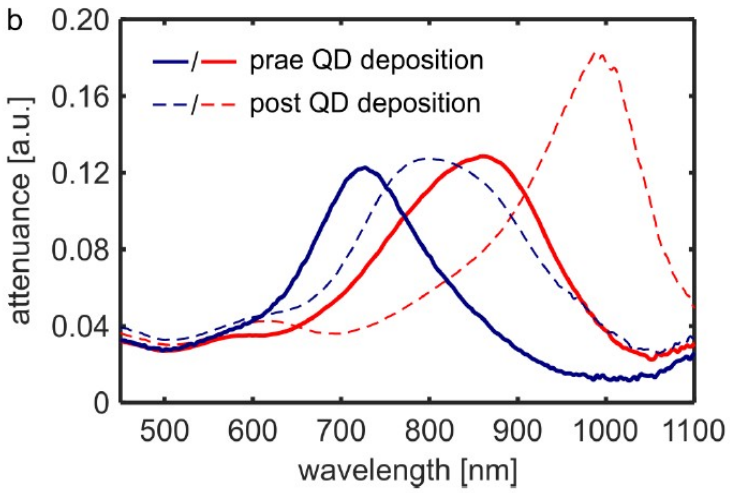
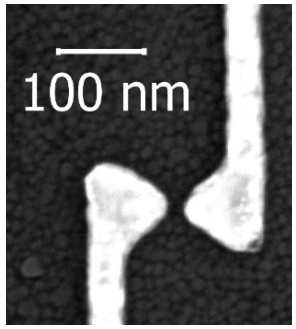
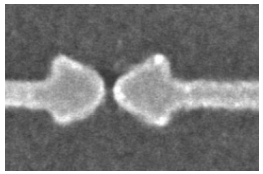


polarization:
longitudinal
transversal





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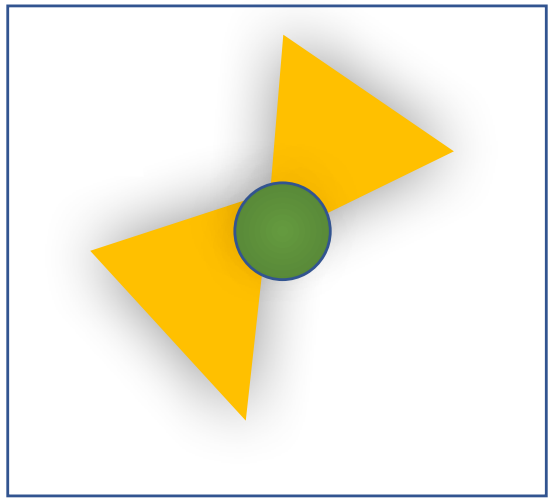
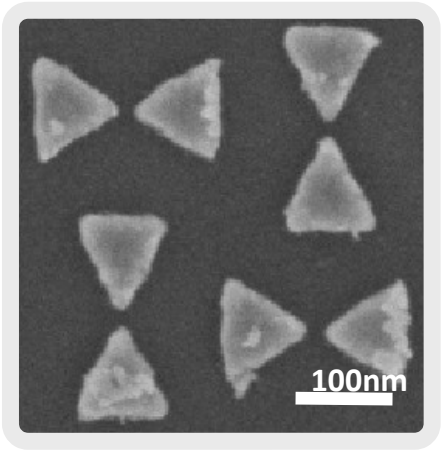
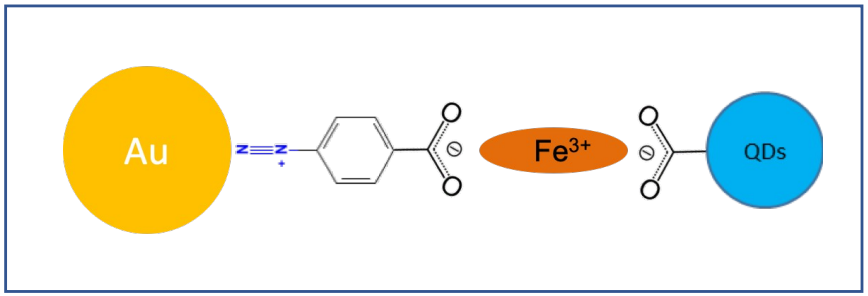
Perspective: regio-selective deposition of QDs in the location of hot-spots





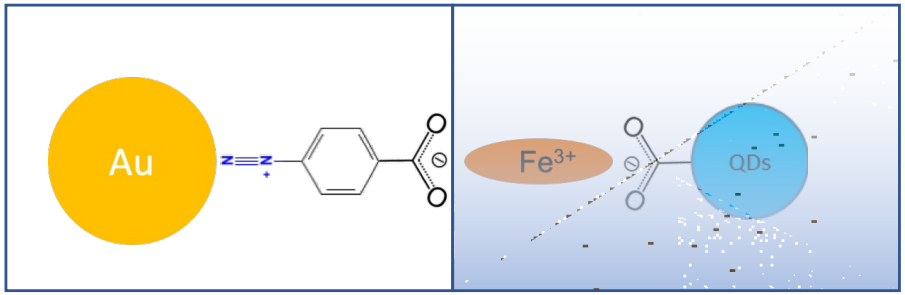
Au bowties fabricated by EBL

Multi-step strategy



Diazonium salt: DCOOH
Cationic iron in solution $Fe3^{+}$
QD negatively charged

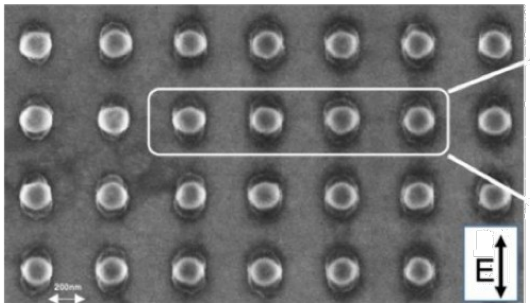
Step 1: regio-selective deposition of QDs in the location of hot-spots

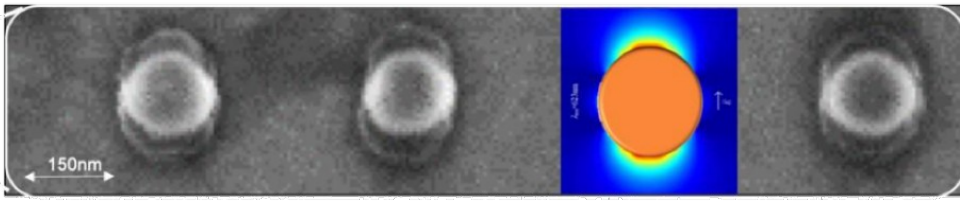


Diazonium salt: DCOOH

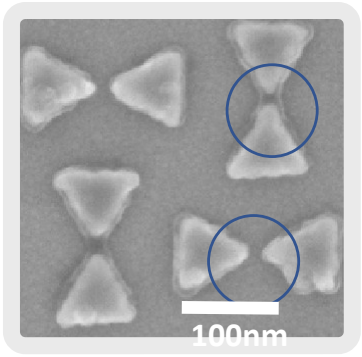
Strategy: hot electron generation: regio-selective grafting uder LSP excitation of poly-aryl films derived from diazonium salts

E

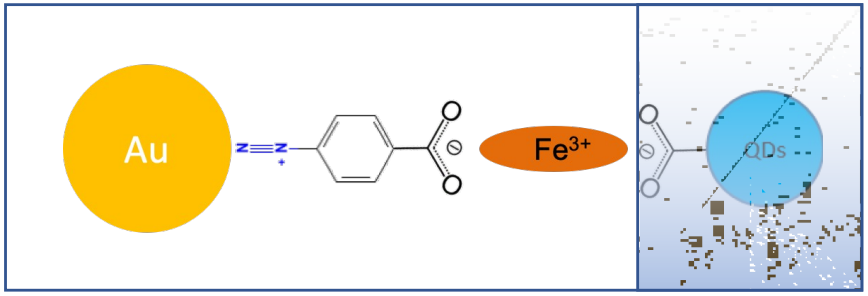


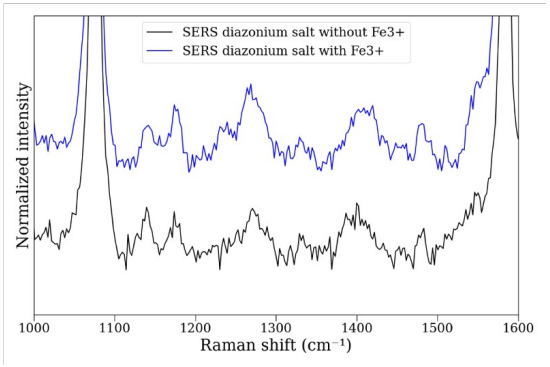


E



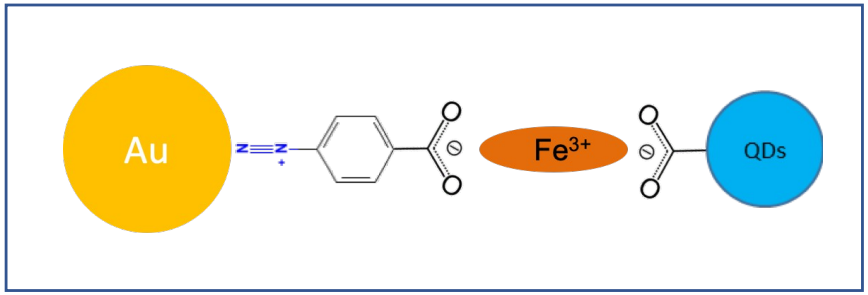
Step 2: addition of $Fe3^{+}$ in the location of hot-spots





SERS spectrum of $DCOO^{-}$ in presence of Fe^{3+}

Step 3: addition of QDs negatively charged in the location of hot-spots (in progress)



PhD thesis : Pascal Cheng (UPC, ITODYS)

Project ANR Advanspec (2022- 2025)

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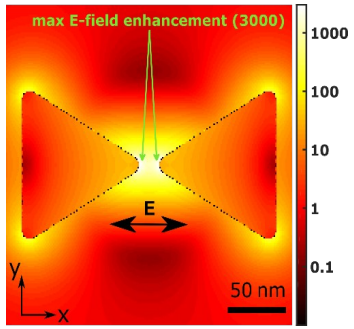

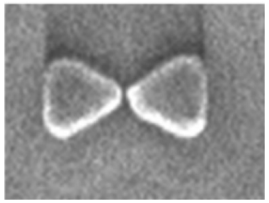

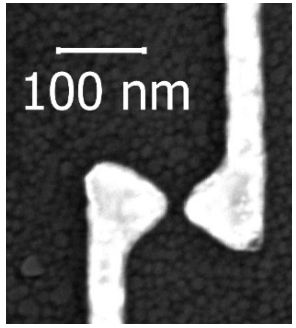

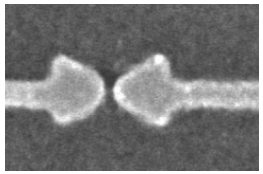

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