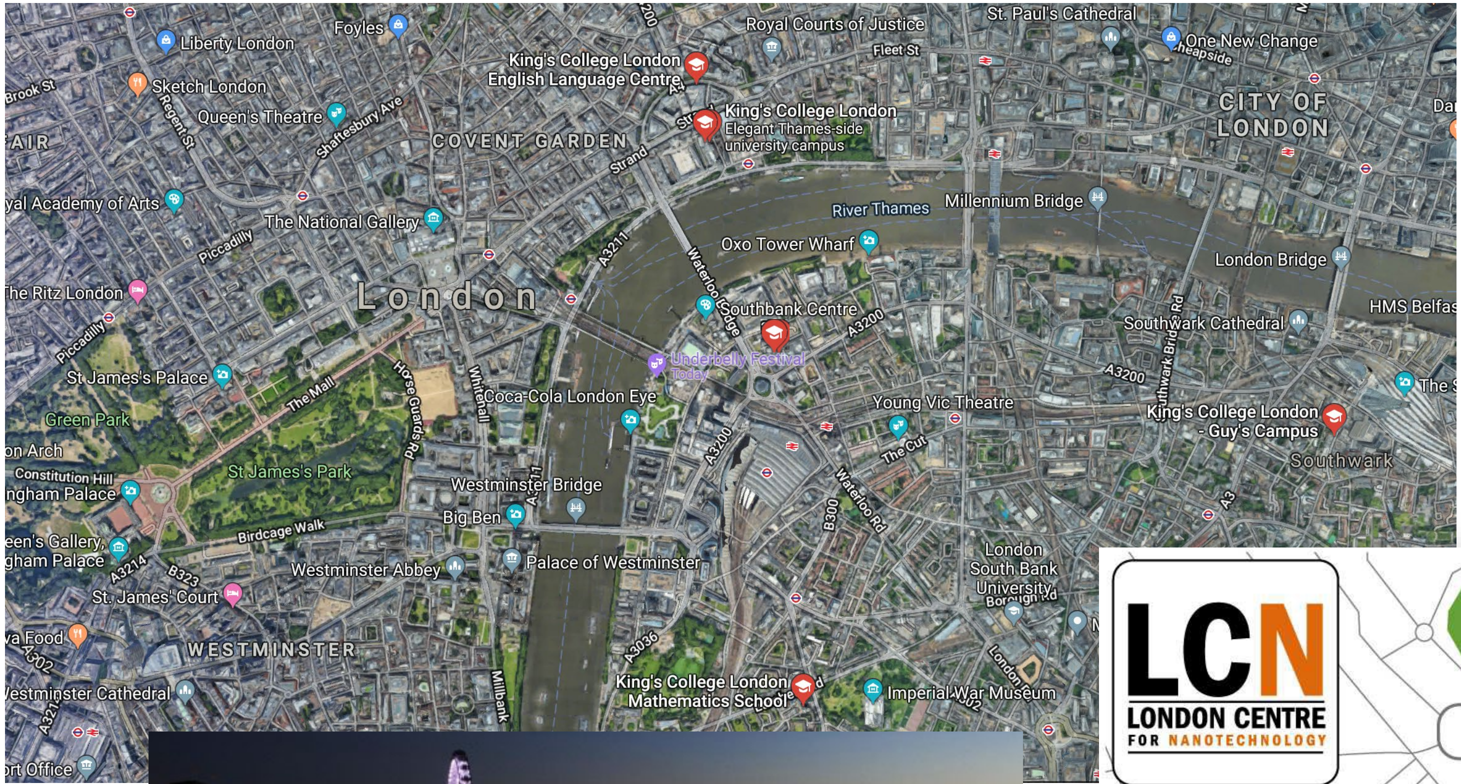
Mastering the nanoscale: approaches to nanomaterial localization, assembly and active control

Sasha Rakovich

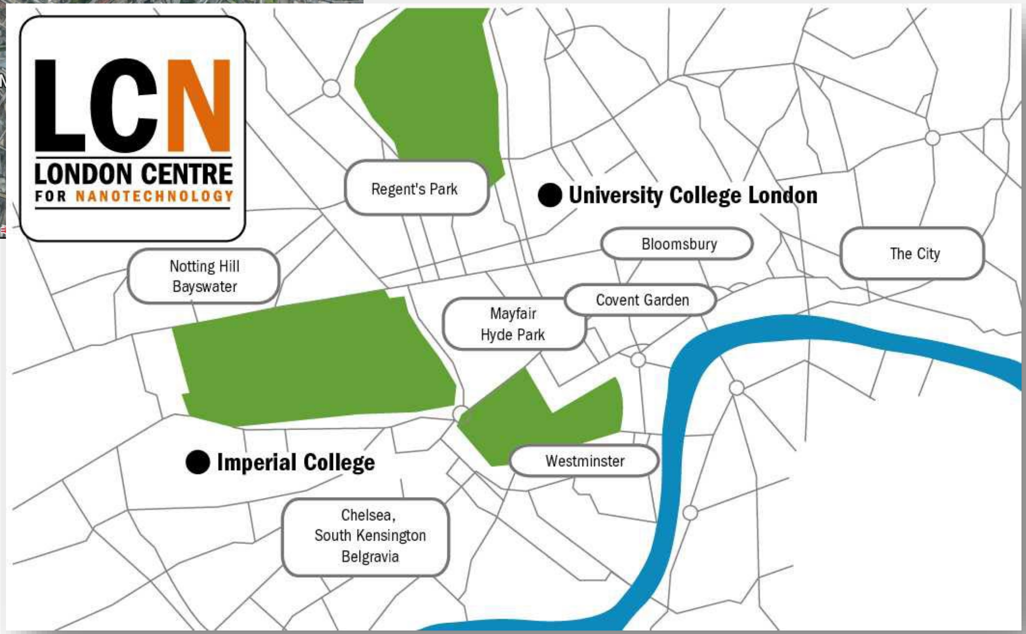
TCD, 15th of March 2024

Slides available here:

Physics@King's College London



- **Photonics & Nanotechnology**
- **Biological Physics & Soft Matter**
- **Theory & Simulation of Soft Matter**
- **Theoretical Particle Physics & Cosmology**
- **Experimental Particle & AstroPhysics**

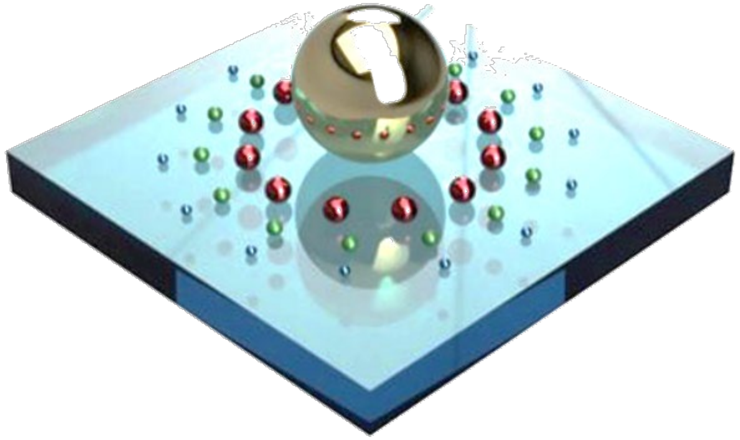


NanoBioPhotonics @ KCL-Physics

Nanophotonics for bioapplications

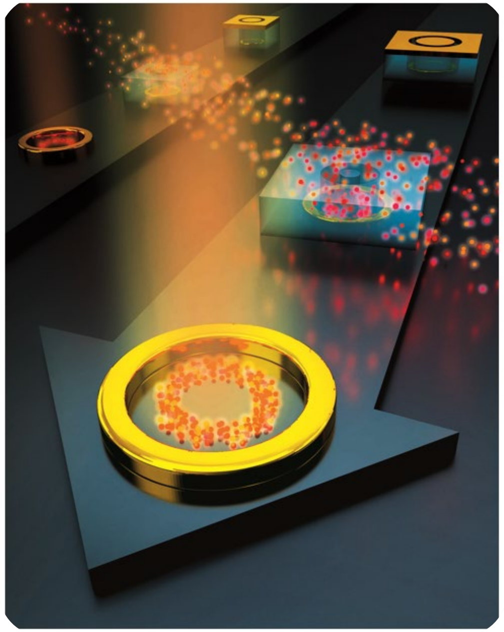
- Plasmonic-based biosensing
- Optical control of analyte motion
- Nanomedicine & theranostics

Nanophotonics for clean energy and sustainability



- Biomimetic light harvesting
- Plasmo-catalysis
- Sustainable fabrication methods

Nanomaterials assembly and control

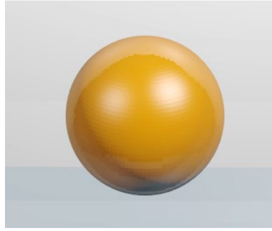


- Self-assembly
- Specific localization
- Control of nanoparticle motion

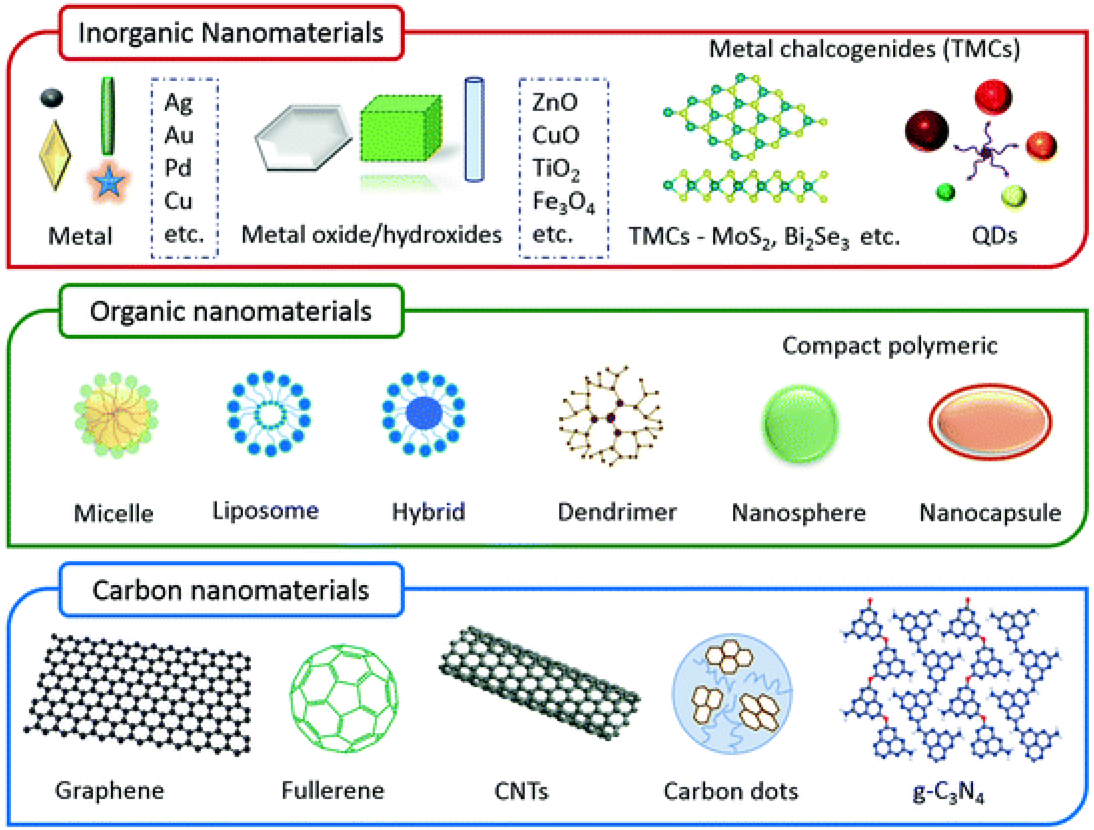
Why colloidal nanomaterials?

Fabrication of nanomaterials

Bottom-up

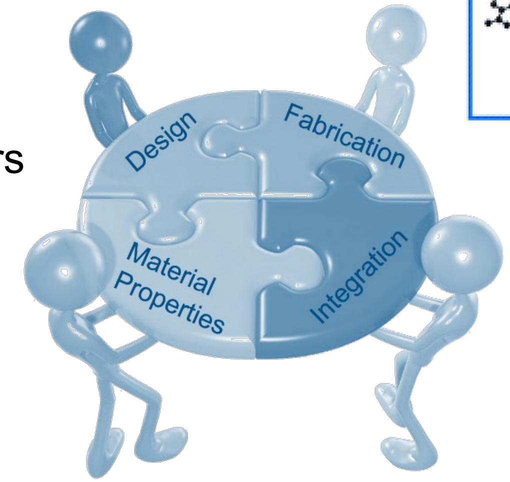


Top-down



Considerations

- Material systems / sizes
- Scalability of fabrication
- Cost of fabrication & precursors
- Reproducibility
- Pre-determined localization
- Compatibility with pre-existing structures



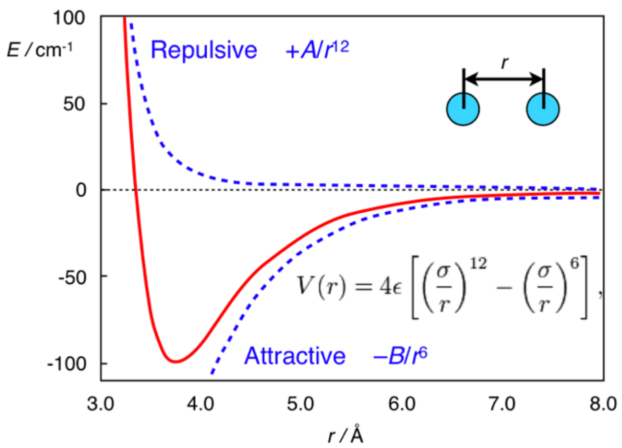
Applications:

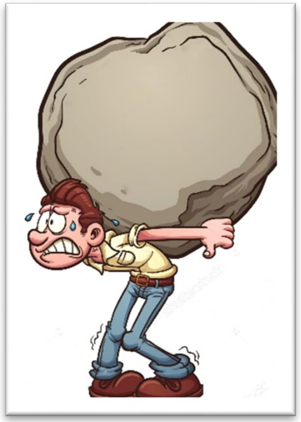
- Renewable energy
- Environment
- Electronics
- Biomedical
- Textiles
- Industrial
- Food
- Agriculture
- Materials for sport

"Synthesis and Functionalization of Nanomaterials", N. Kumar, S. S. Ray, Springer

Material immobilization toolbox

Long-range attractive forces



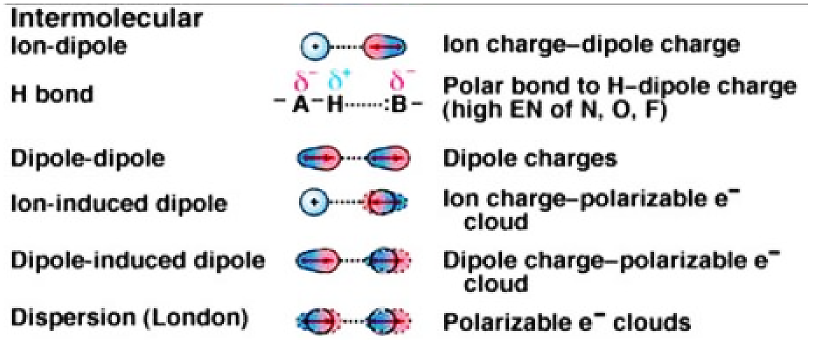


Delivery

+

Fixation

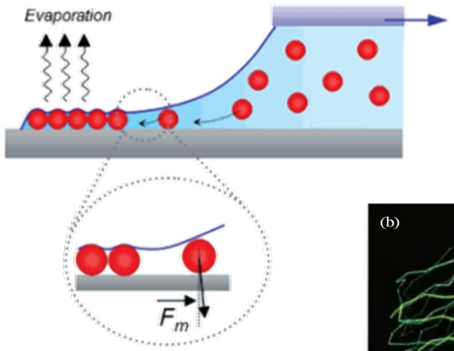
Intermolecular forces



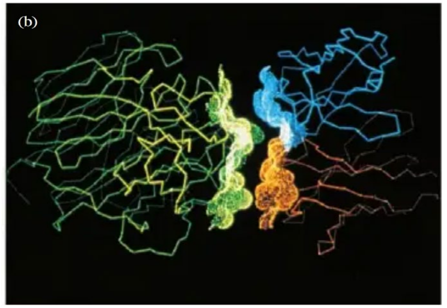
Other driving forces

- Electrostatic
- (Di-)electrophoretic
- Brownian motion
- Gravity
- Optical
- Convective
- Capillary

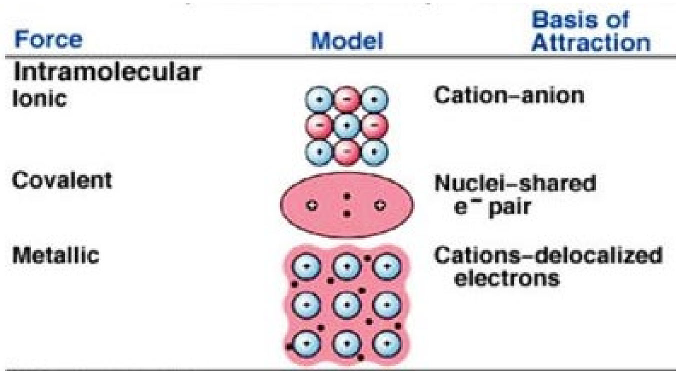
Typically more than type contributes



Malaquin, Langmuir 23, 11513 (2007)



Intramolecular forces



cscsdashaicechem.weebly.com

Kuby Immunology. Ed. J.A. Owen, J. Punt, S.A. Stranford. 7th edition, W. H. Freeman and company, New York (2013)

Outline

Introduction

Control of nanomaterials for applications

Self-assembled systems

Nano-bio hybrids

Plasmonic superclusters

Deterministic localization of NPs

QDs coupling to plasmonic structures

Large area localization of metallic NPs

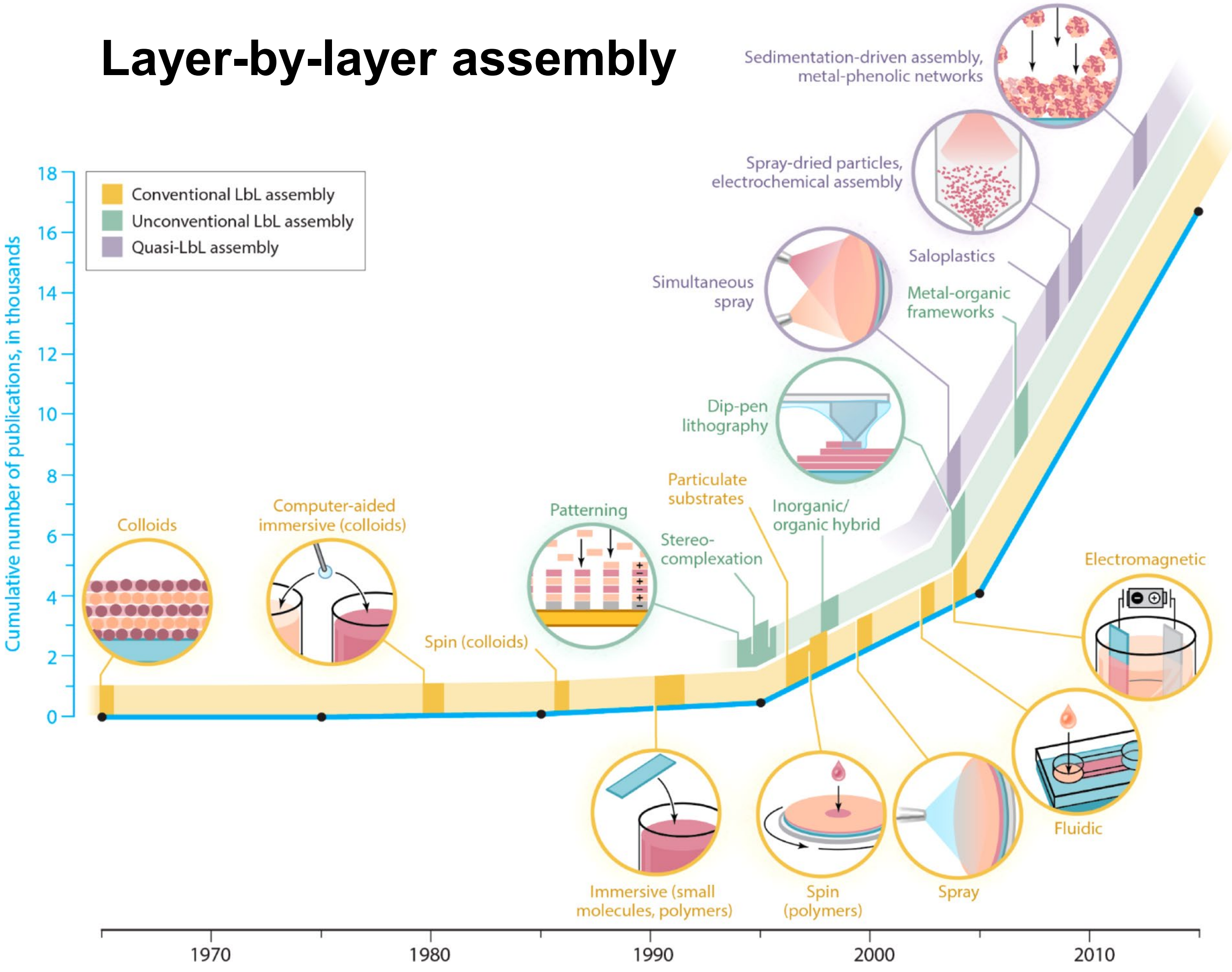
Active control of NPs

Exploiting Brownian motion for long range transport

Conclusions

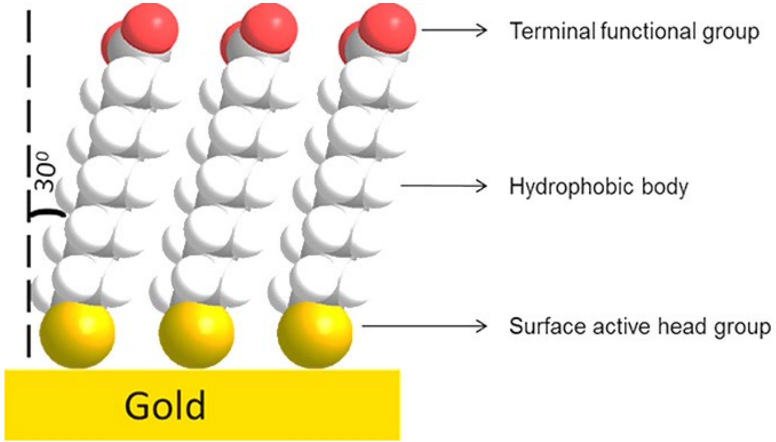
Self-assembly

Layer-by-layer assembly



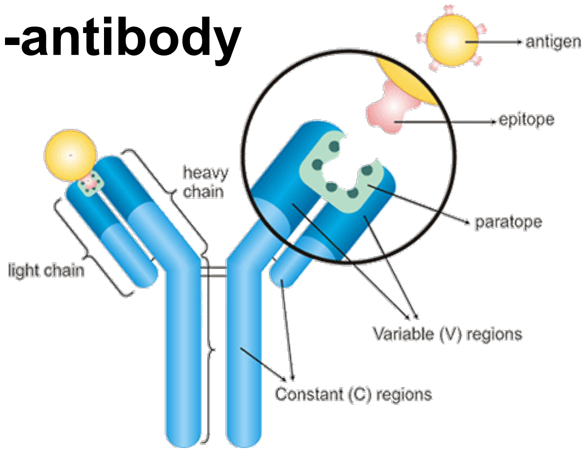
DOI: 10.1021/acs.chemrev.6b00627
Chem. Rev. 2016, 116, 14828−14867

SAM formation



https://www.intechopen.com/books/carbohydrate/self-assembled-monolayers-of-carbohydrate-derivatives-on-gold-surfaces

Antigen-antibody binding

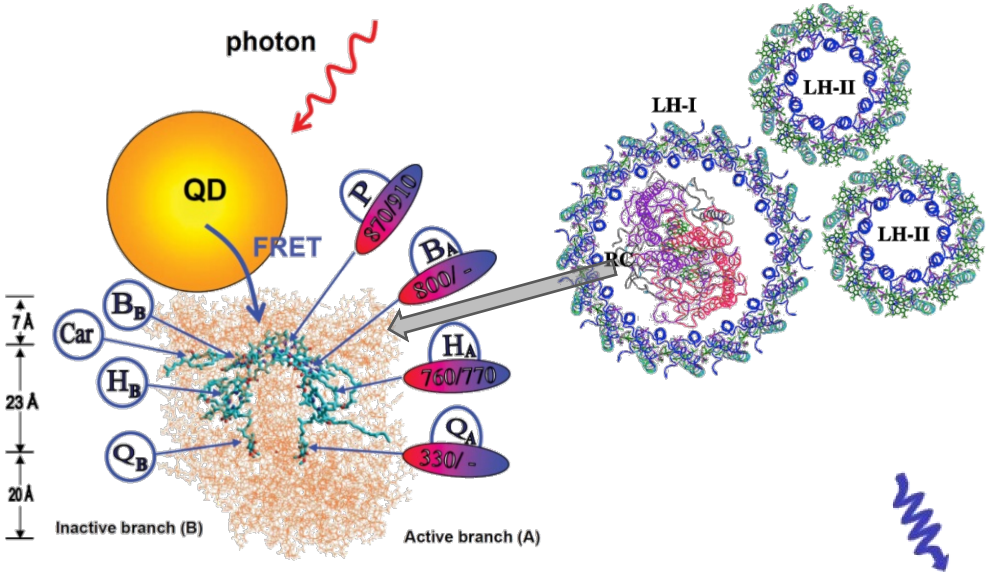


https://www.cusabio.com/c-21045.html

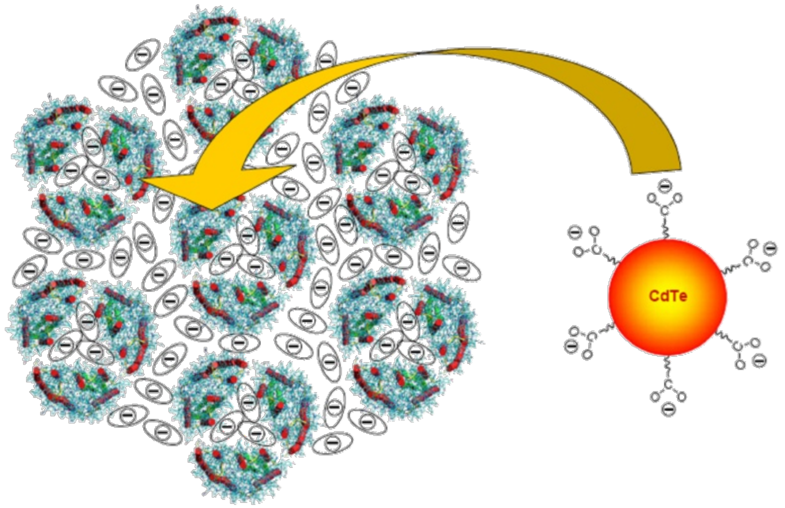
Self-assembly of nano-bio hybrids

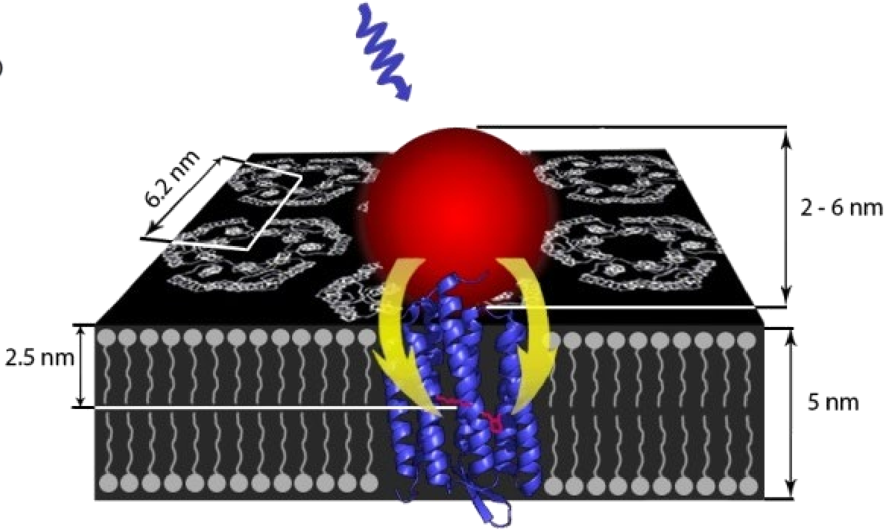
Biomaterials:

- Typically have many amino acids
- In solutions, some of end groups can be charged
- In many cases, electrostatic self-assembly with colloidal NPs is possible



Assembly of QDs with bacterial reaction centres





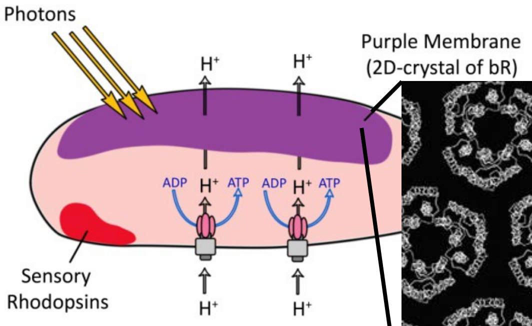
Assembly of QDs on Purple Membranes containing bR protein

NanoLetters **10**, 2640 (2010)

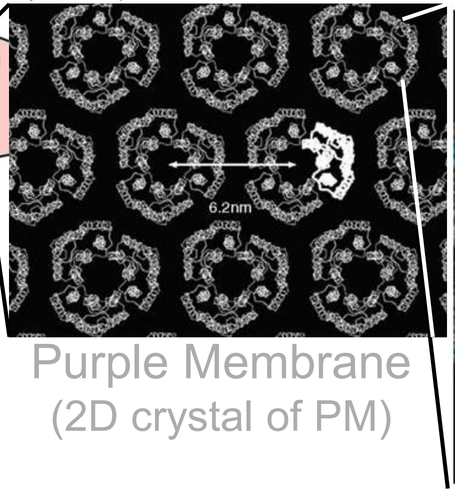
QDs as artificial antenna for bacteriorhodopsin protein

Membrane protein with:

- Photoelectric properties
- Photochromic properties
- Charge transport properties

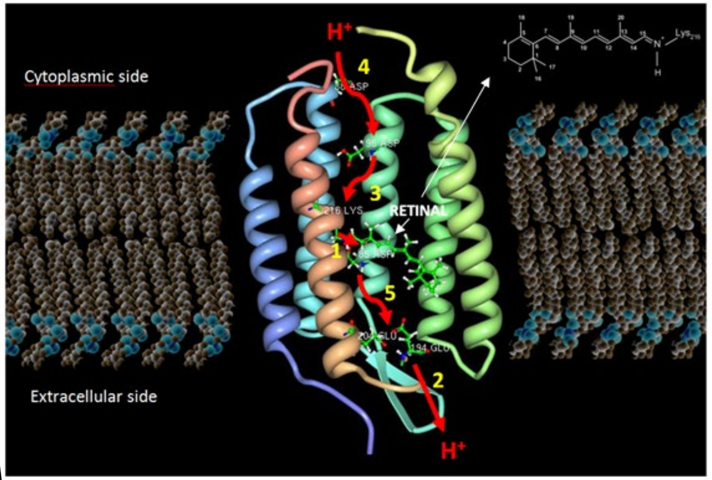


Halobacteria



Purple Membrane
(2D crystal of PM)

Bacteriorhodopsin protein
(light-activated proton pump)



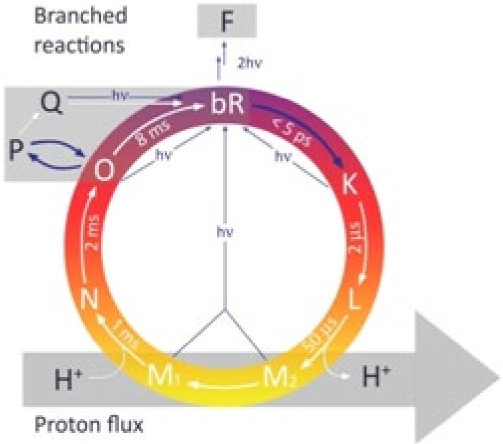
Performance optimised by evolution:

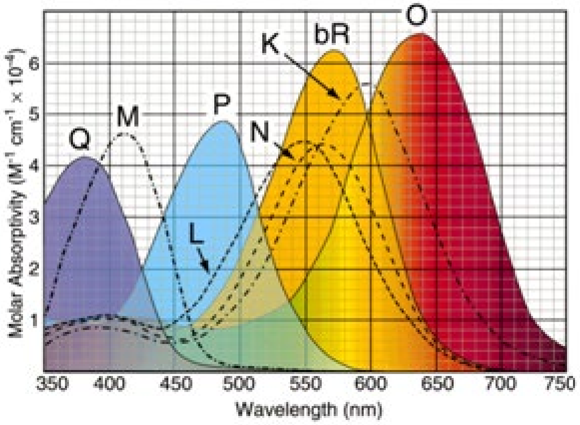
- High photo- chemical and thermal stability
- High fatigue resistance

Not able to deal with UV-photons:

- Can destroy light-absorbing molecule
- Utilizes only 0.1-0.5% of solar light

Use QDs as artificial down-converting LH antenna



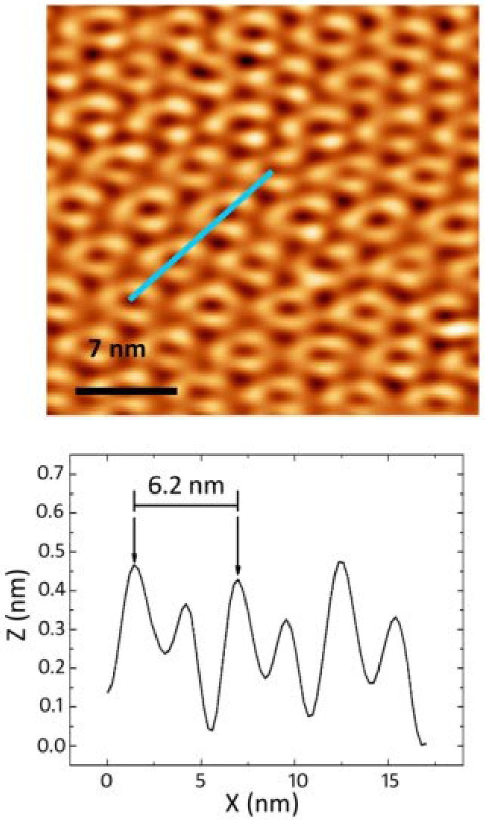


Adapted from Birge et al. J. Phys. Chem. B 103, 10746 (1999)

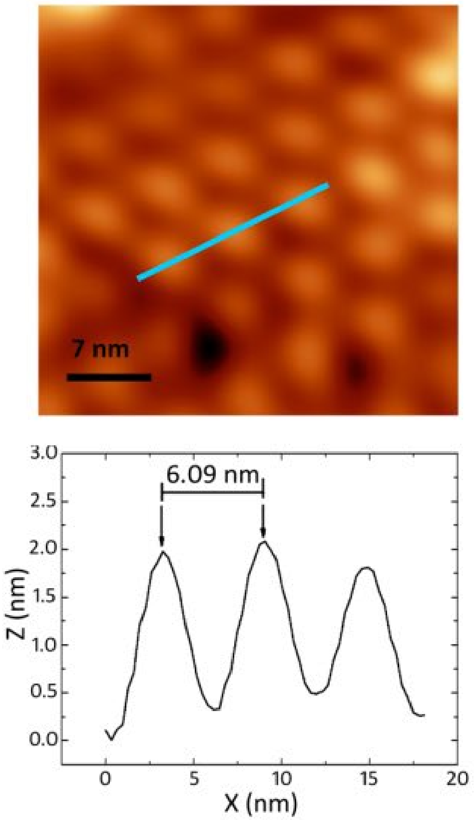
QDs as artificial antenna for bacteriorhodopsin protein

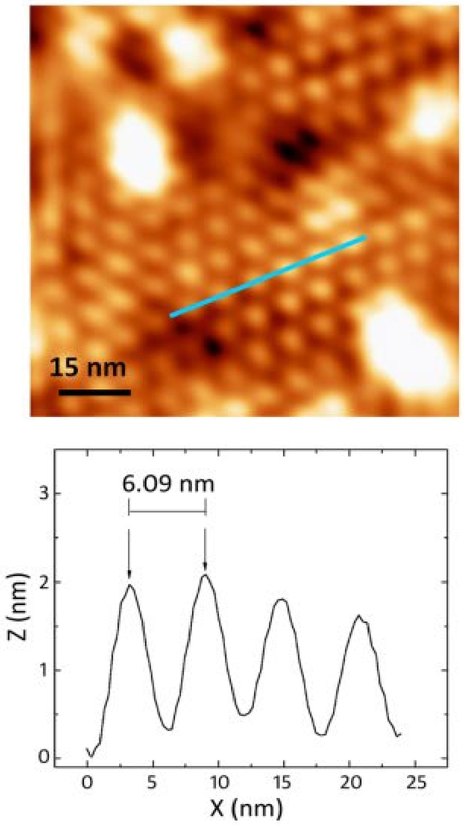
Electrostatic self-assembly of QDs on Purple and White Membranes

bR membrane

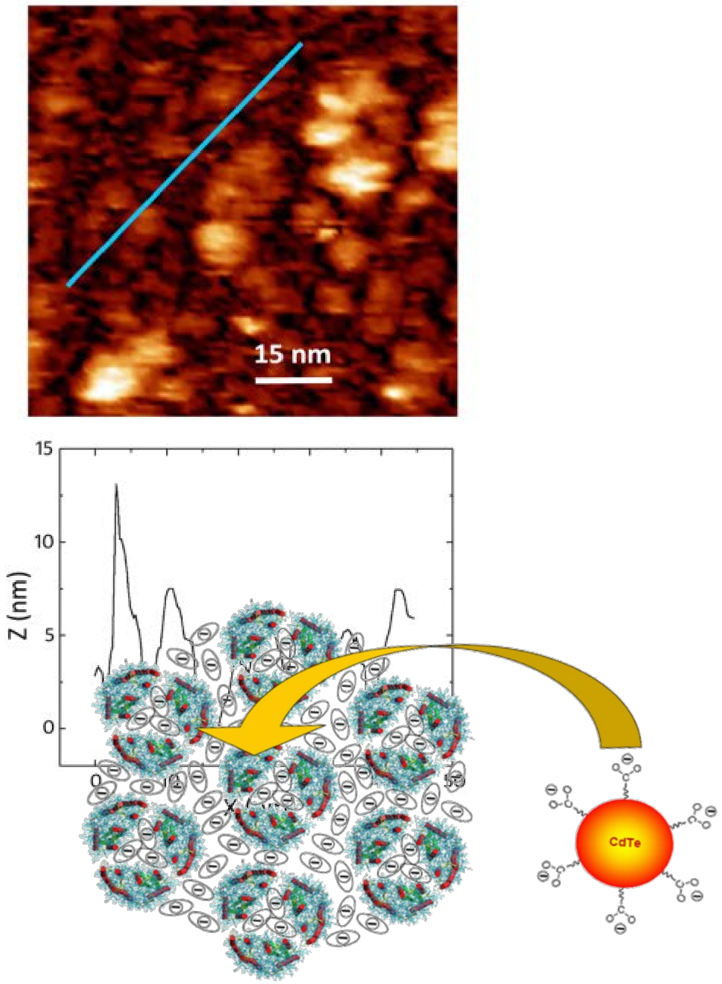


6 nm hydrodynamic radius QDs

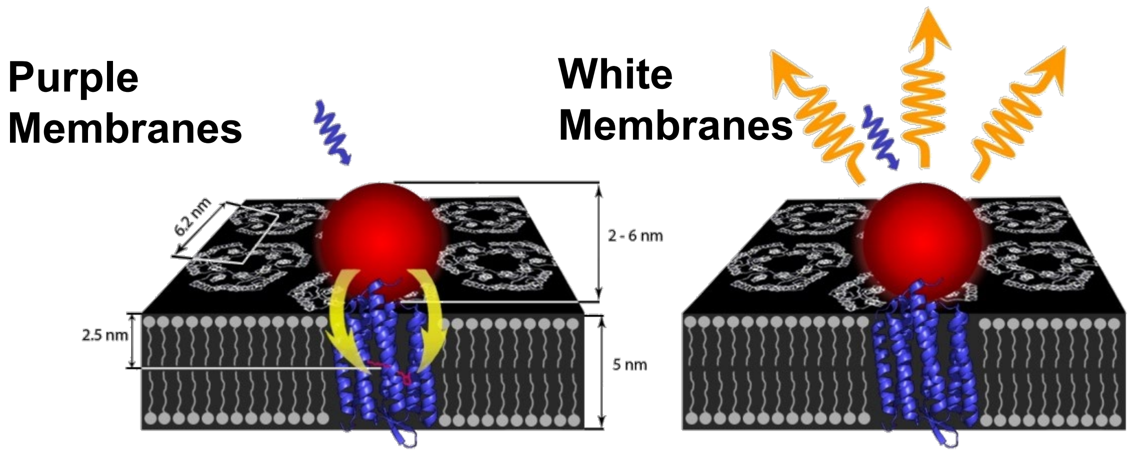


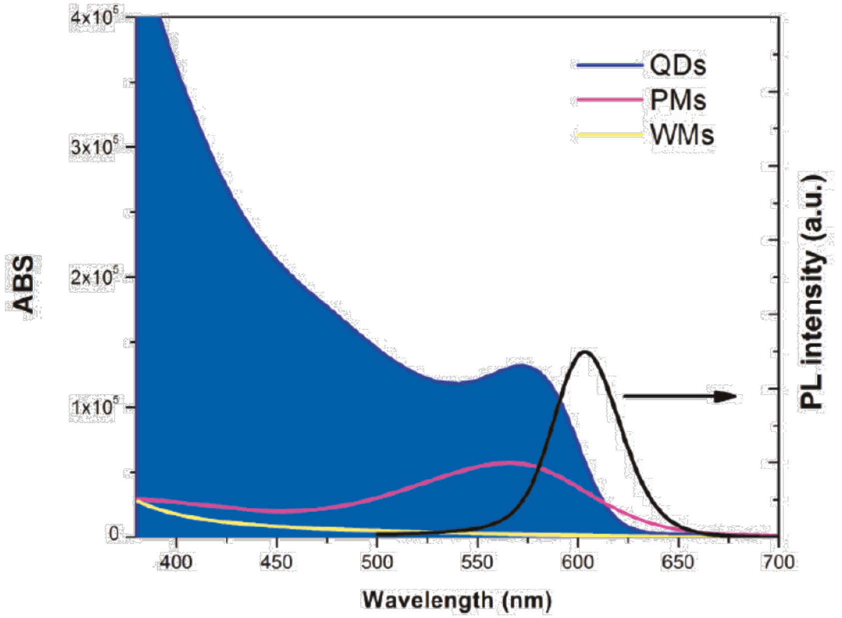


Typical, high density

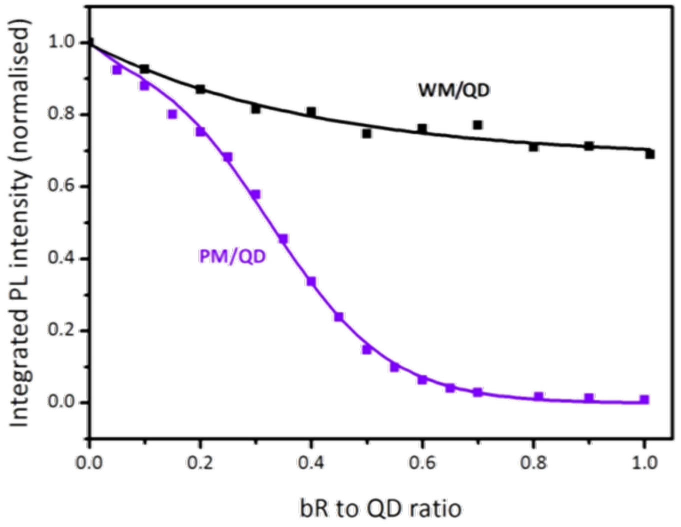


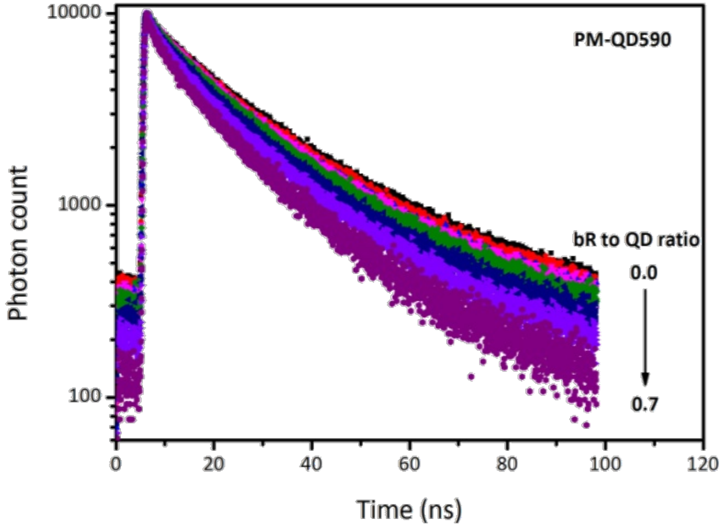
QDs as artificial antenna for bacteriorhodopsin protein

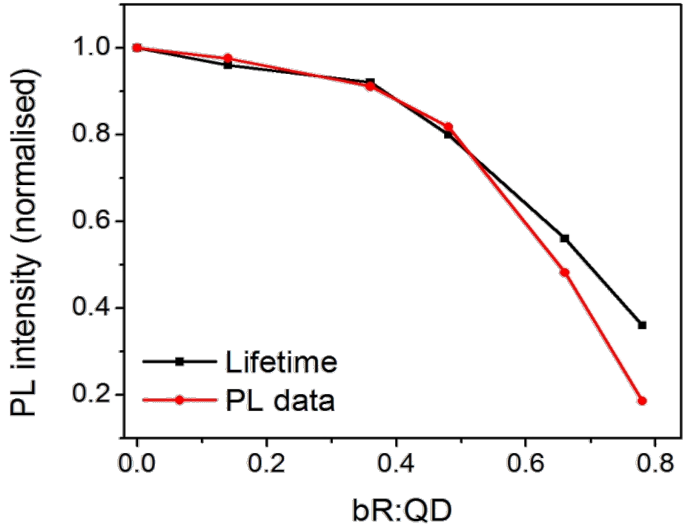




Energy transfer in QD-PM complexes



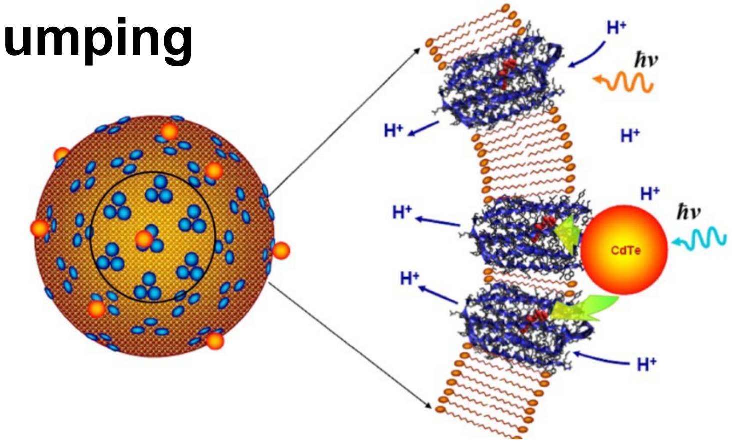


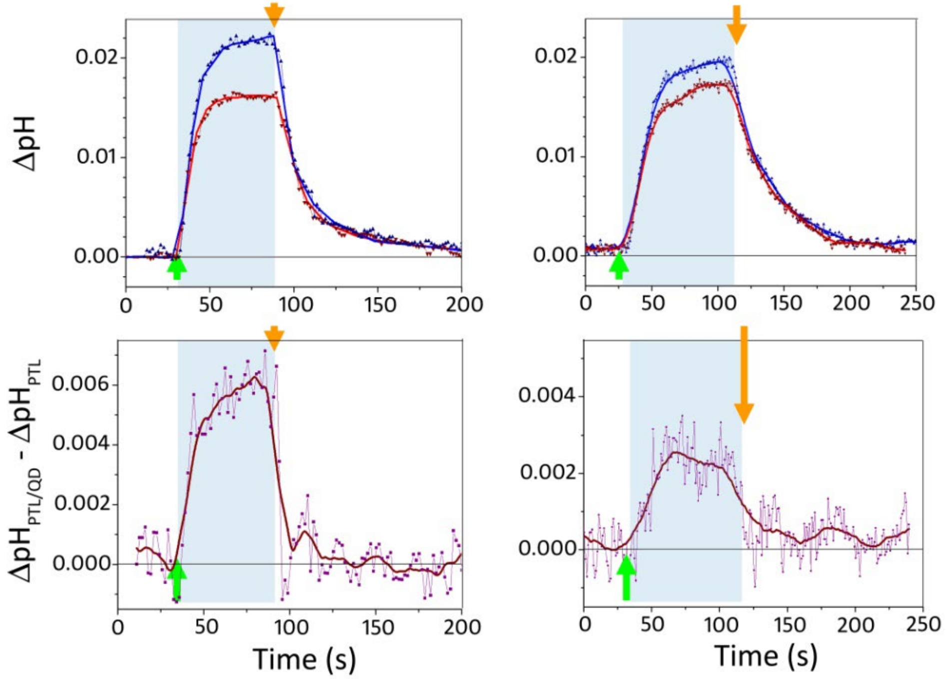


Introduction
Self-assembly
Nano-bio hybrids
Superclusters
Localization
2-step EBL
Template dissolution
Active control
Brownian ratchets
Conclusions

QDs as artificial antenna for bacteriorhodopsin protein

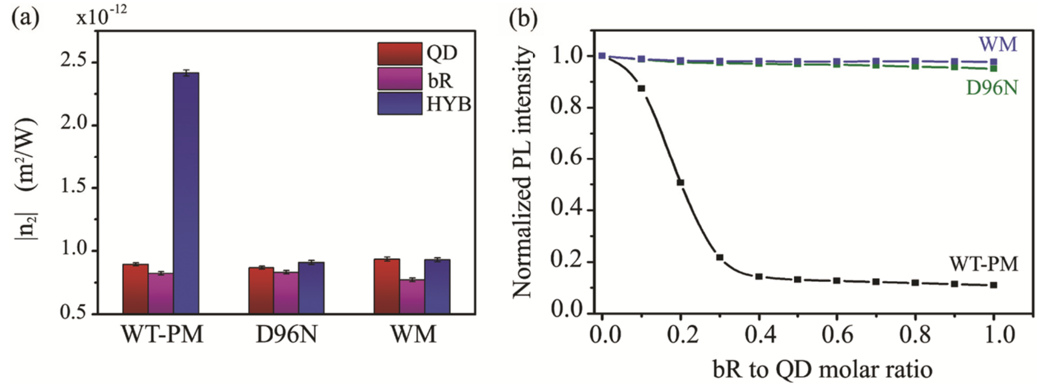
bR proton pumping efficiency

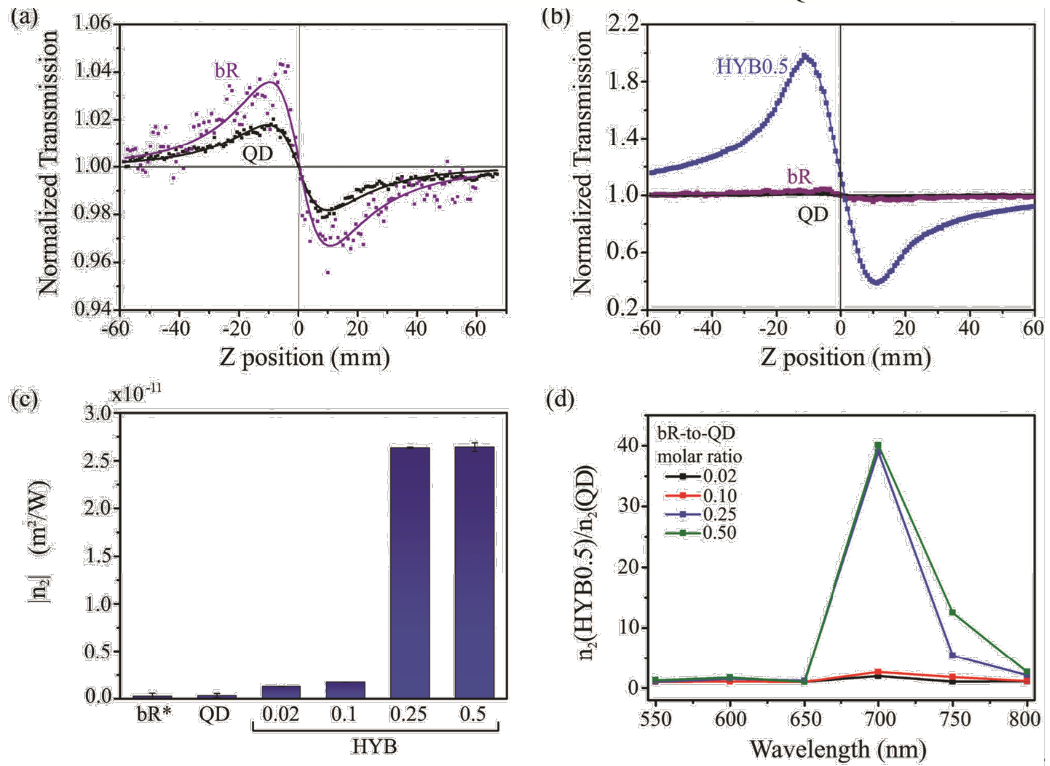




A. Rakovich *et al.*, NanoLetters **10**, 2640 (2010)

Nonlinear refractive index

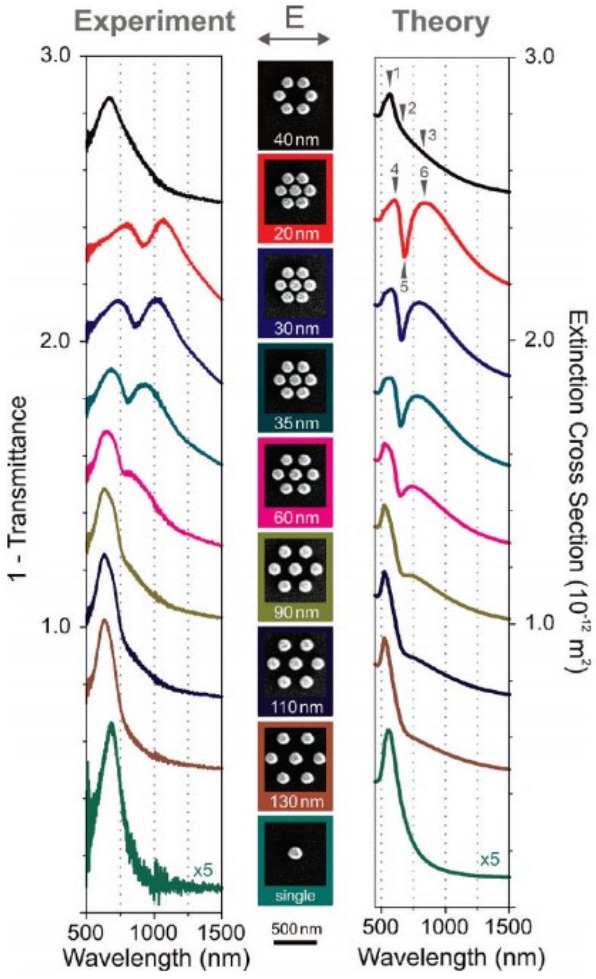




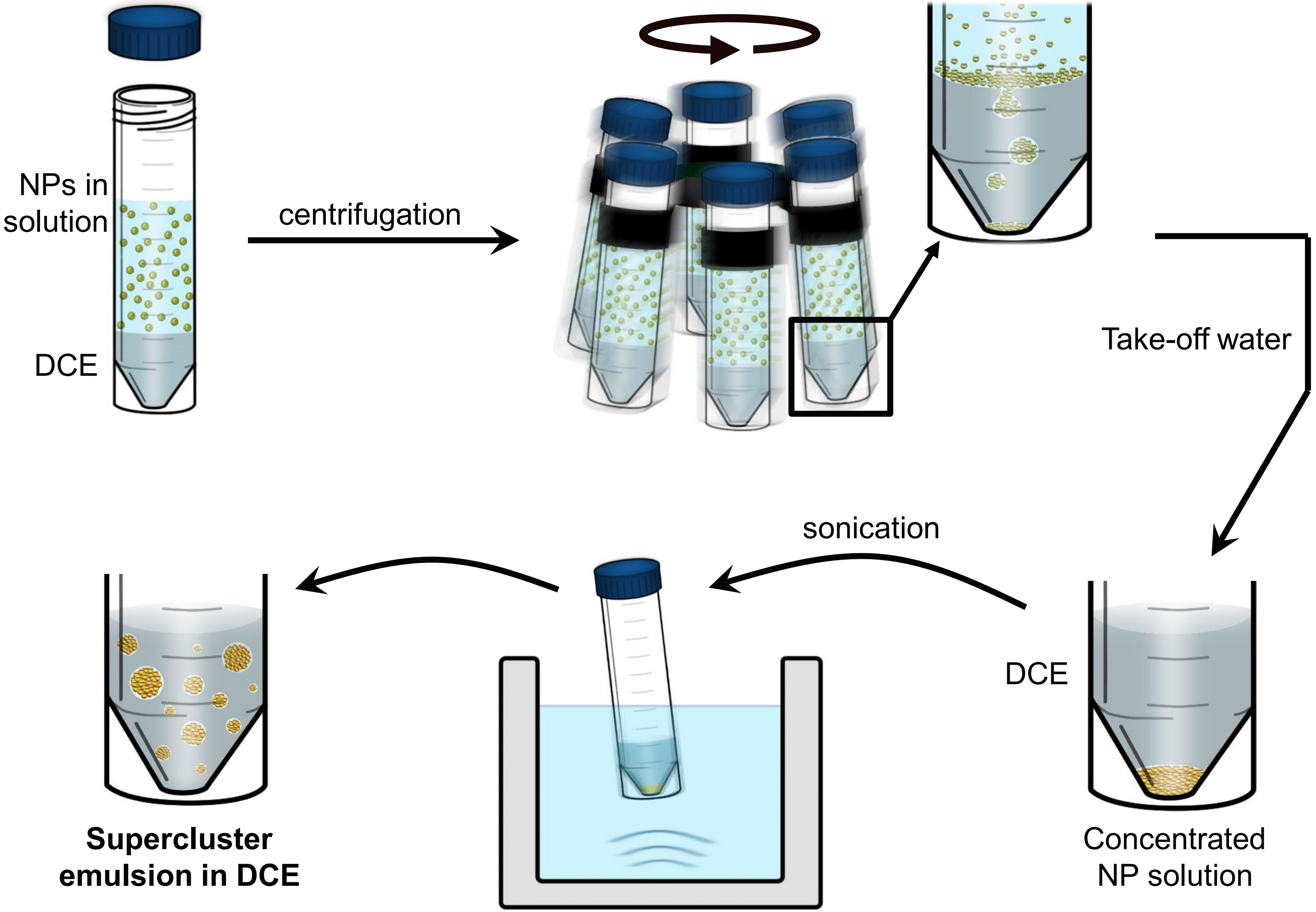
A. Rakovich *et al.*, ACS Nano 7, 2154-2160 (2013)

Self-assembly of metallic superclusters

Based on hydrophobic effect



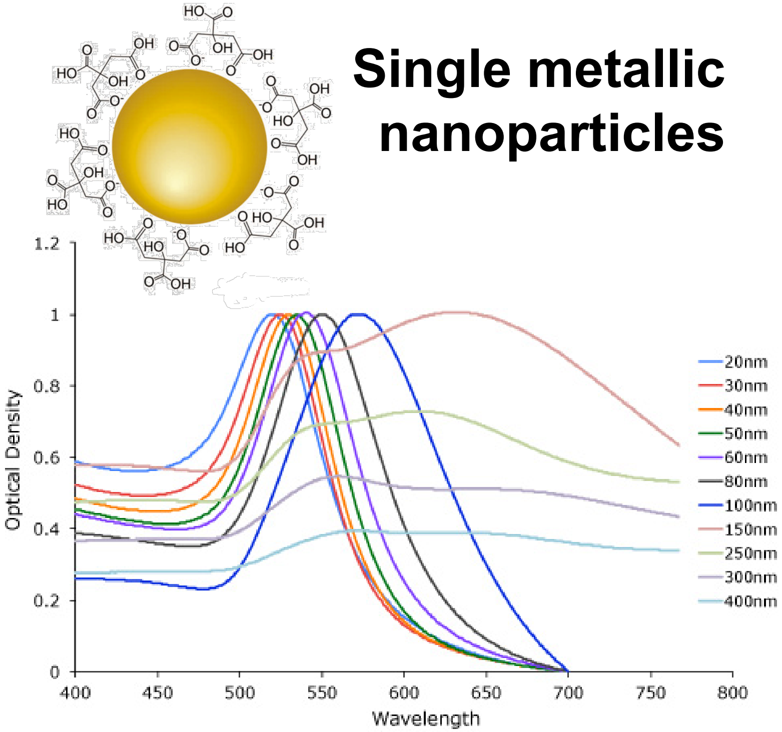
NanoLetters 10, 2721 (2010)



A. Lauri et al. ACS Photonics 4, 2070-2077 (2017)

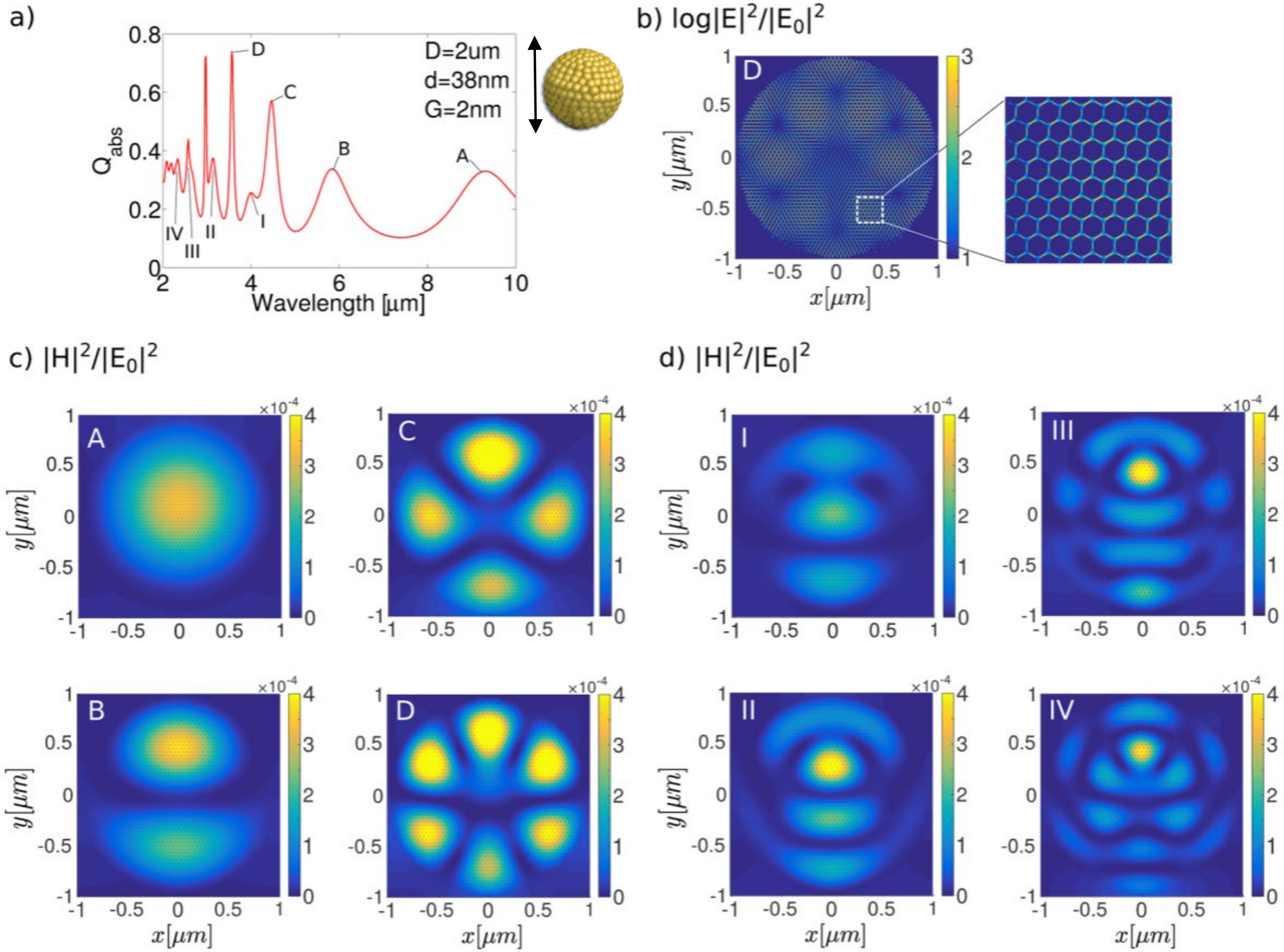
Properties of metallic superclusters

Single metallic nanoparticles



http://www.cytodiagnostics.com

Superclusters of metallic nanoparticles

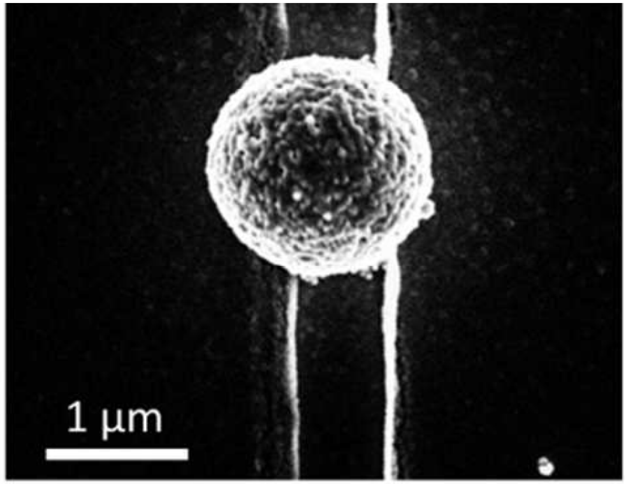


V. A. Turek et al. ACS Photonics 3, 35-42 (2016)

Introduction
Self-assembly
Nano-bio hybrids
Superclusters
Localization
2-step EBL
Template dissolution
Active control
Brownian ratchets
Conclusions

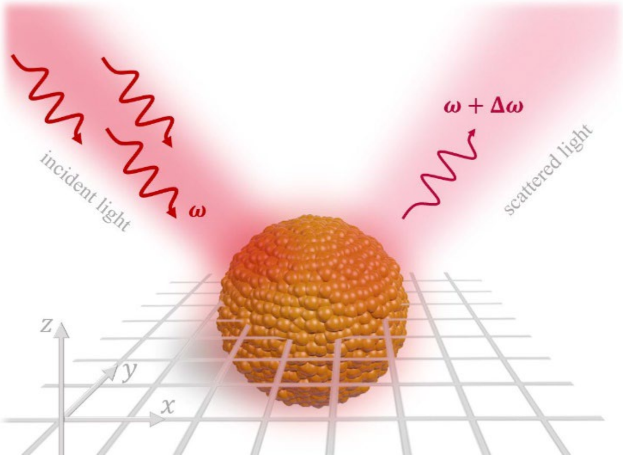
Experimental verification of collective modes

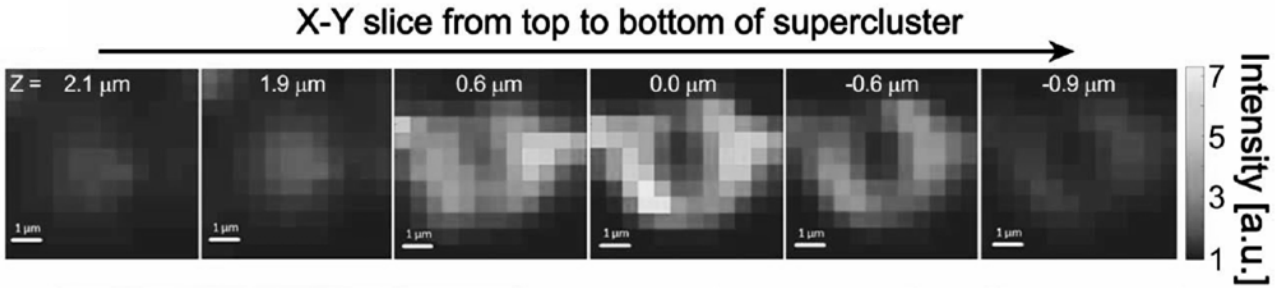
TEM: cluster size

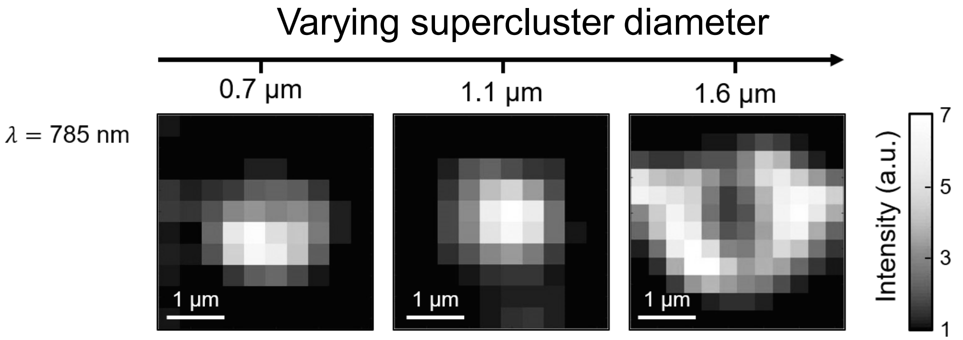


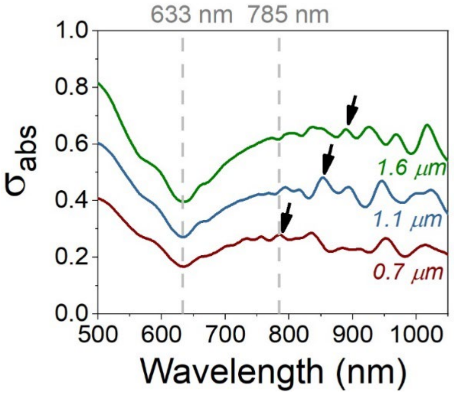
Raman: modal map

4-MBA self-assembled onto Au NPs prior to supercluster formation

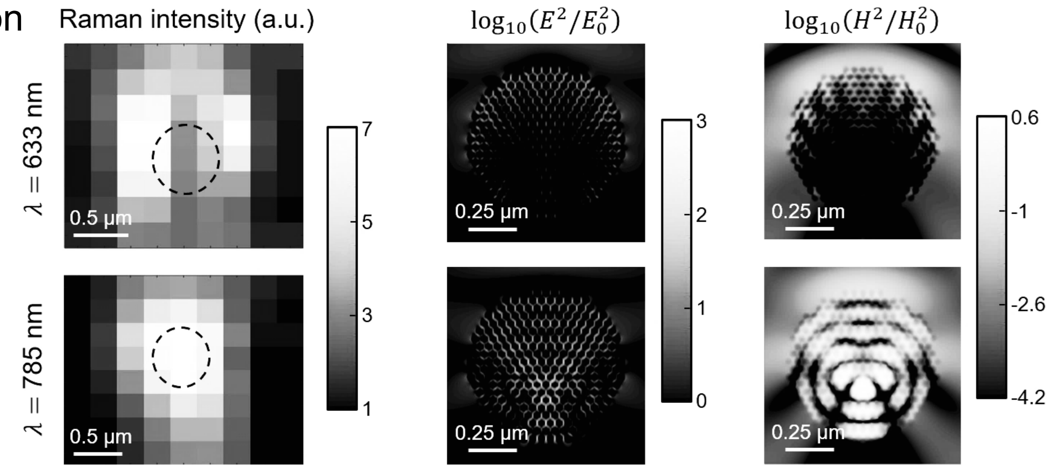








Varying excitation wavelengths D = 0.7 μm:

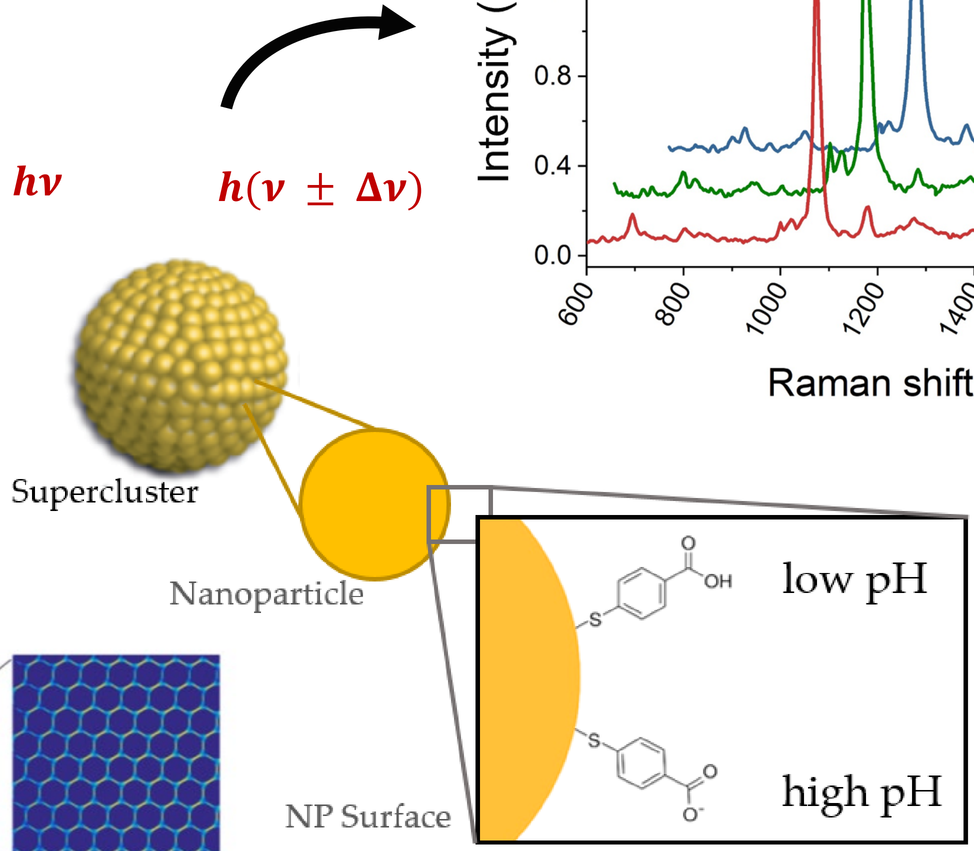


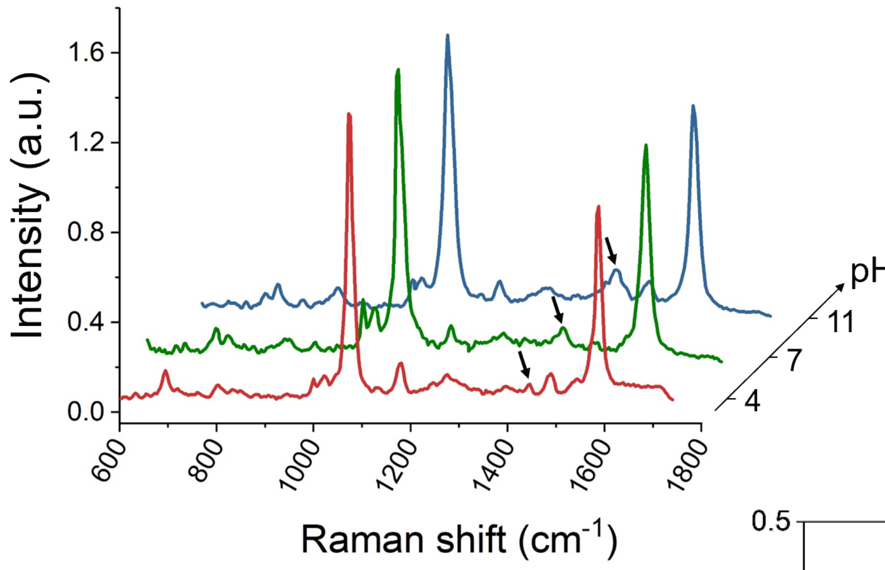
V. A. Turek et al. ACS Photonics 3, 35-42 (2016); *A. Lauri et al.* ACS Photonics 4, 2070-2077 (2017)

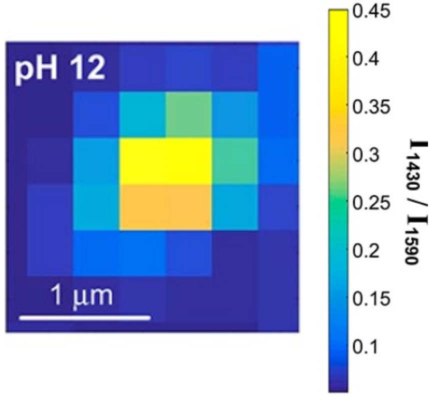
Sensing with metallic superclusters

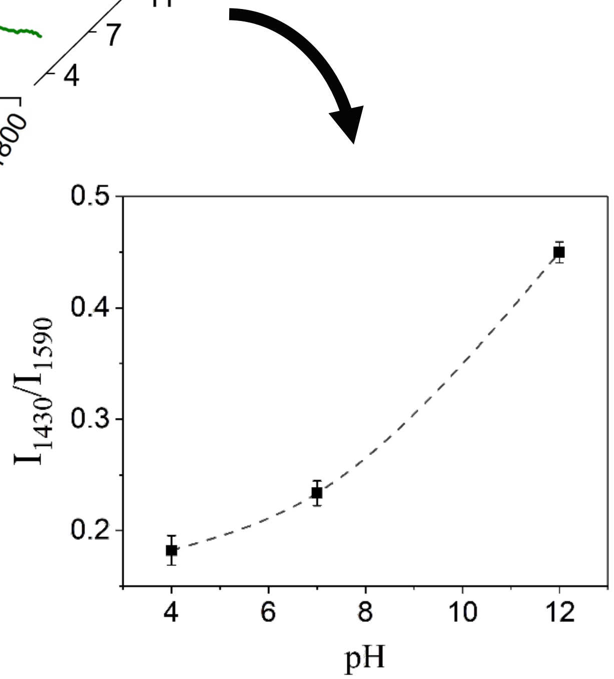
Varied pH of solvent

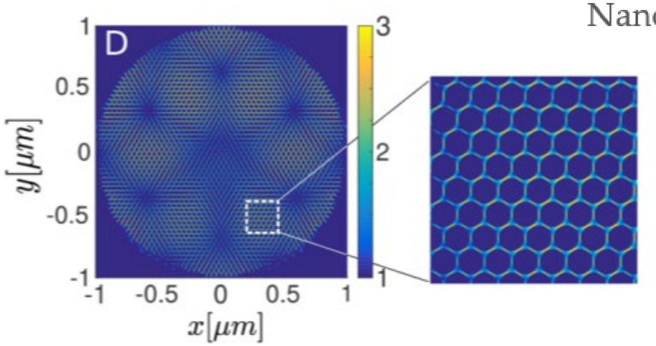
causing de-/re-protonation of carboxylic acid group on the 4-MBA molecule











A. Lauri et al. ACS Photonics 4, 2070-2077 (2017)

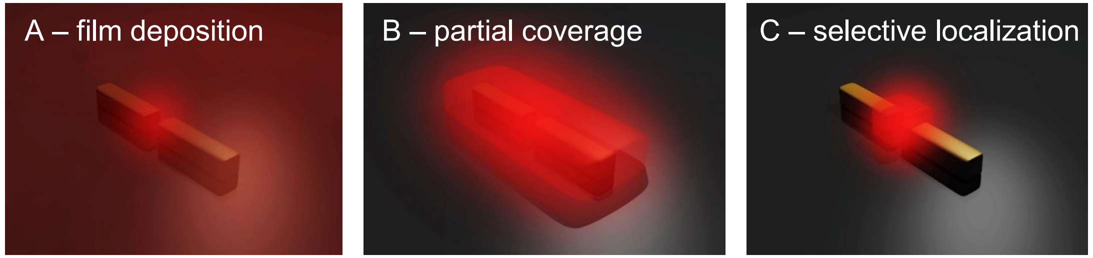
Selective localization for as-designed fabrication

Tendency towards interdisciplinary science
- Exploit properties of different materials

Drive for device minimisation & integration
- Avoid cross-talk of different components
- Nanoscale control of materials

Independent design of components
- Time-efficiency
- Collaborative efforts

Reproducibility of performance
- Chemo- & photo- stability of components
- Reproducible characteristics



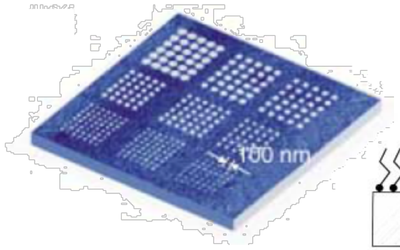
Introduction
Self-assembly
Nano-bio hybrids
Superclusters
Localization
2-step EBL
Template dissolution
Active control
Brownian ratchets
Conclusions

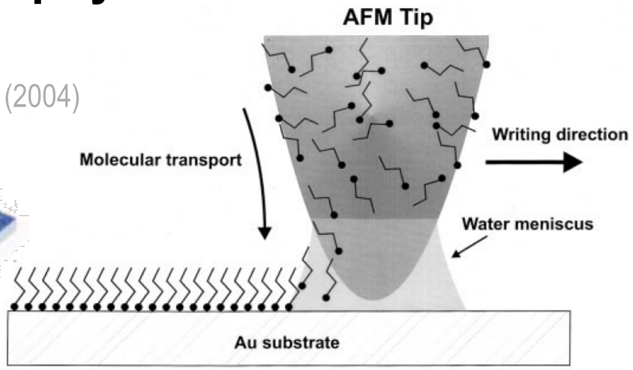
Selective localization methods

Technique	Advantages	Disadvantages
Directed self-assembly	• Fast • Large area coverage • Works on almost any substrate	• Weak adhesion • Use of non-removable masks
SAM patterning	• Good precision	• SAM covers entire substrate • Slow due to large area exposure
MACE-ID	• Good control over amount deposited • OK precision	• Precursor in EBL chamber • Use of additional material as scaffolding (no functional purpose)
Multi-step EBL	• OK precision • Very flexible	• Use of masks (can leave residues)
AFM-based techniques	• High precision	• Slow and labour intensive • SAM cover entire substrate • Difficult to do on samples with pre-existing structures
Localised polymerization	• High precision • No mask	• Deposition of additional material (polymer matrix) • Only works with resonator structures
LAMI-based approach	• Very high precision • "In-built" localisation • No mask	• Low yield • No mask: non-specific attachment can be an issue • Only works with plasmonic structures
Hot-carrier driven chemistry	• High precision • "In-built" localisation • No mask	• Chemistry difficult to control • Localisation not only in hotspot • Only works with plasmonic structures
Optical printing	• Moderate precision • No mask • Very strong attachment	• Labour intensive • Difficult to do with pre-existing structures • Functionalisation of entire substrate

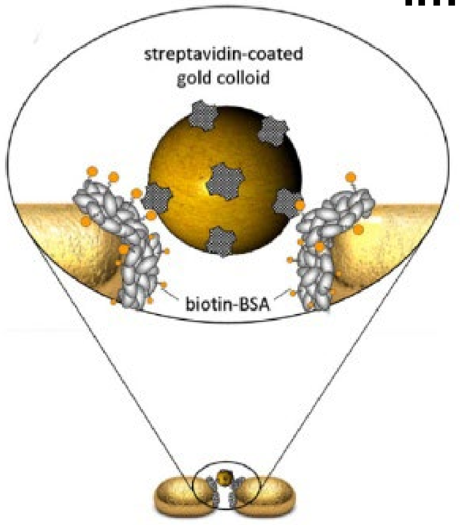
Dip-pen lithography

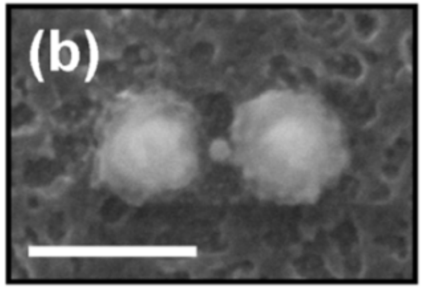
D. S. Ginger *et al.*
Ang Chem Int Ed 43, 30-45 (2004)





Light-activated molecular immobilization (LAMI)-based approach

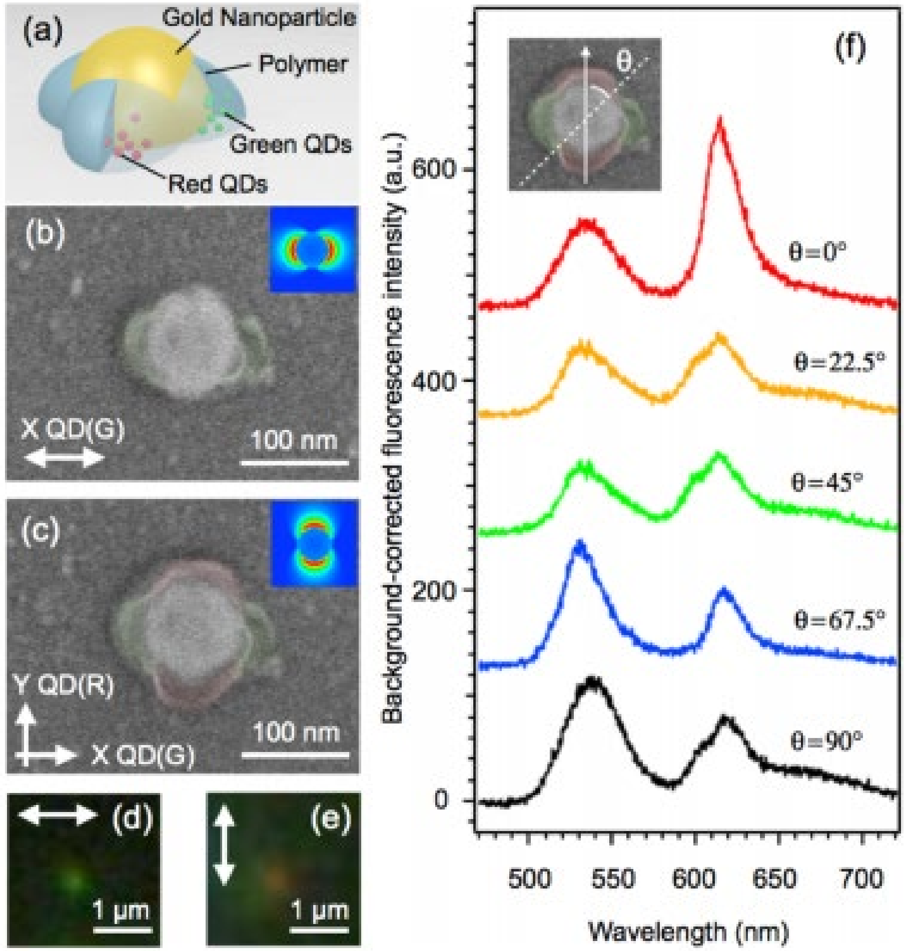




C.M. Galloway *et al.*
NanoLetters 13, 4299 (2013)

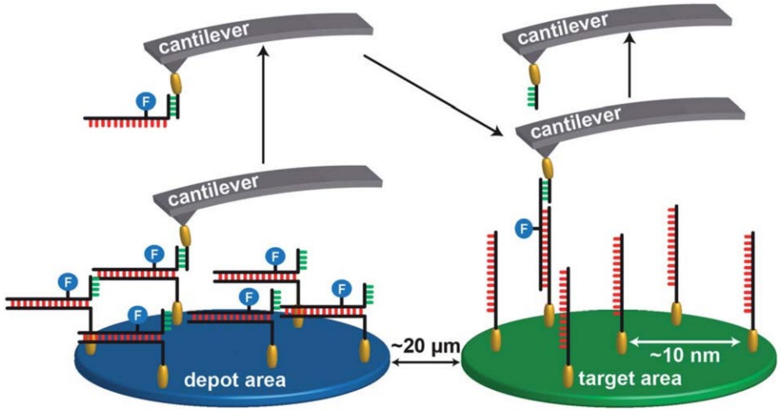
Deterministic localization methods

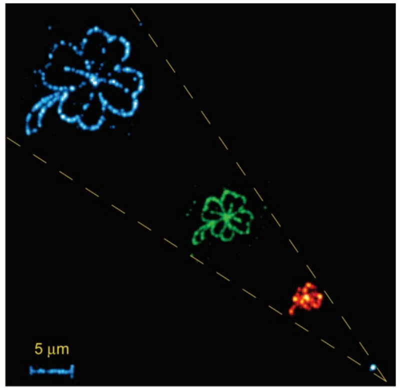
Photopolymerization



Zhou, Nano Lett. 15, 7458-7466 (2015)

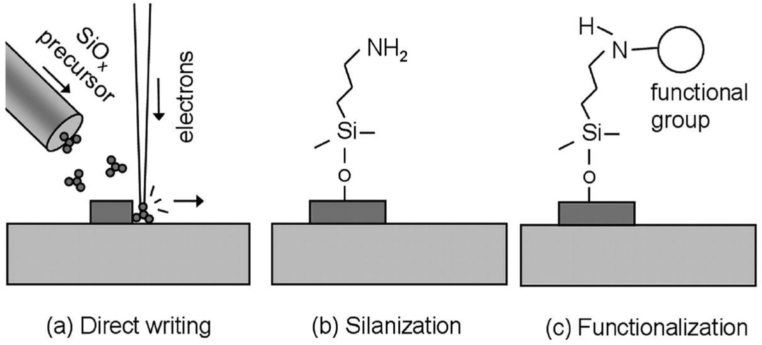
Cut and Paste

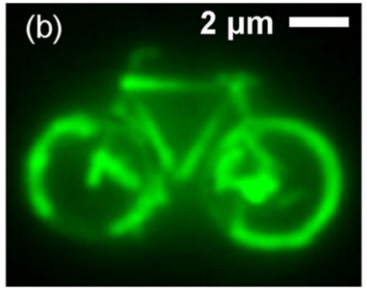




Jacobs, Chem. Sci. 5, 1680 (2014)
Puchner, NanoLetters 8, 3692-3695 (2008)

MACE-ID



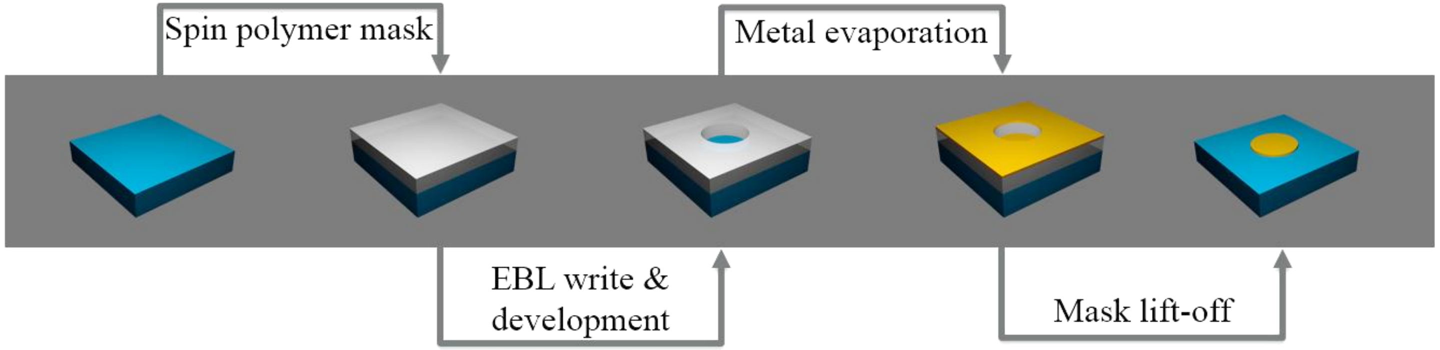


W. Slingenbergh, ACS Nano 6, 9214 (2012)

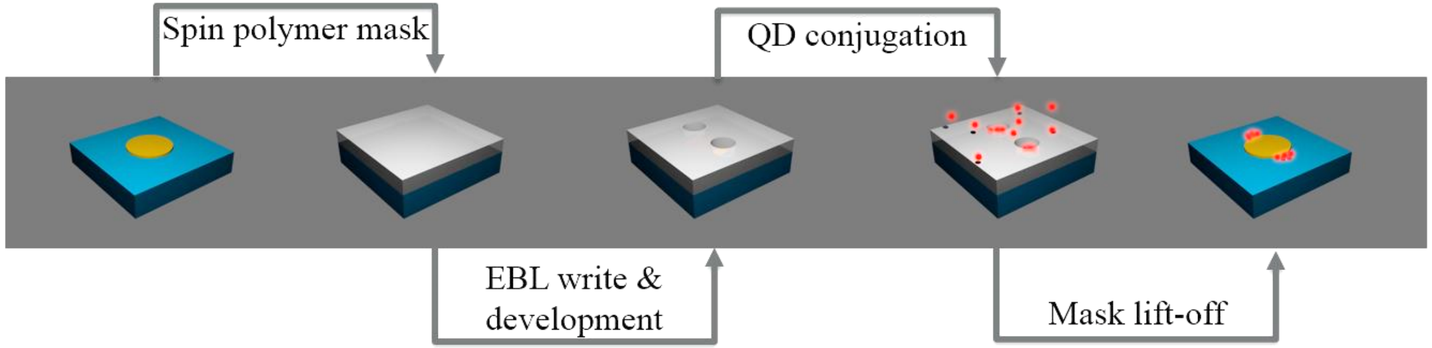
2-step EBL method

For localization of QDs in regions of interest near pre-existing structures

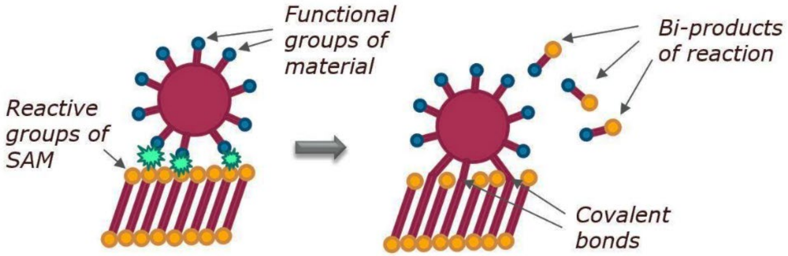
Step 1: fabrication of nanoantenna



Step 2: selective localisation of NPs



QD attachment step



SAM formation:

- Alkane-thiols and derivatives (e.g. 1-amino undecanethiol) for metals, some semiconductors
- Ethoxysilanes and derivatives (e.g. APTES) for oxygen- or silicon terminated surfaces

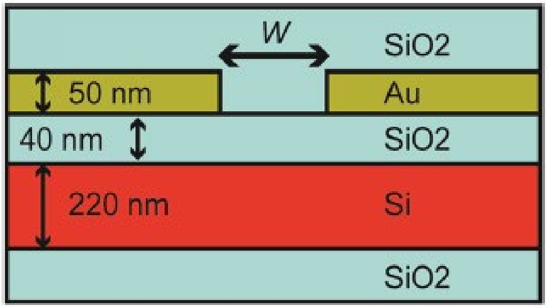
QD conjugation to SAMs

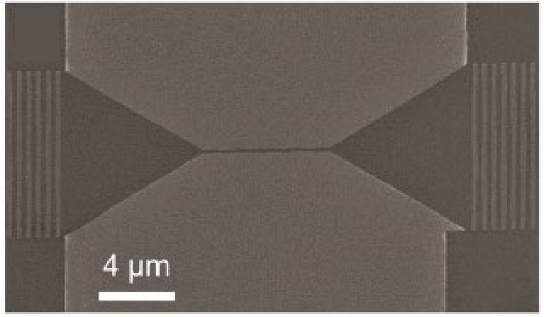
- Covalent conjugation, e.g. via EDC-coupling reaction
- Antigen-antibody linkage

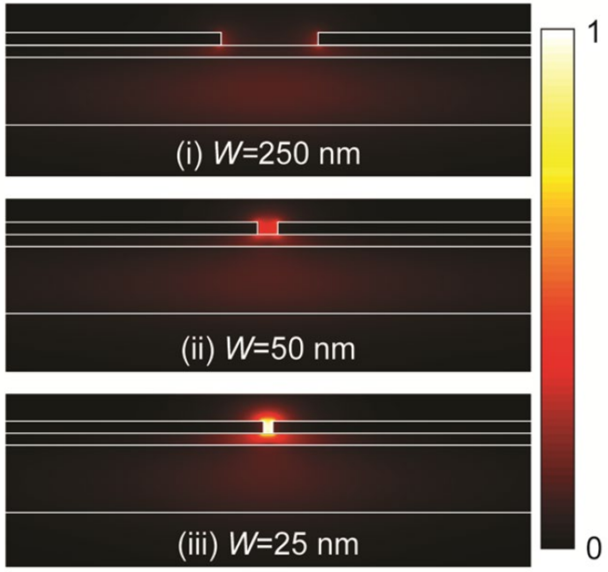
Introduction
Self-assembly
Nano-bio hybrids
Superclusters
Localization
2-step EBL
Template dissolution
Active control
Brownian ratchets
Conclusions

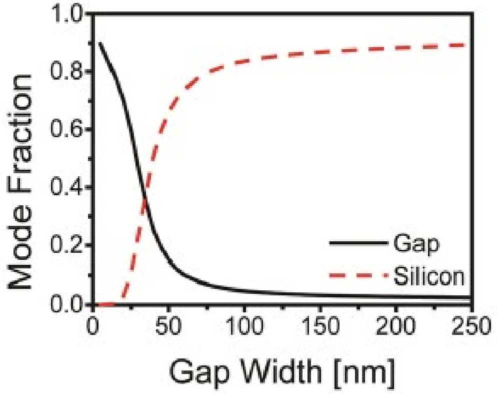
Application of the 2-step EBL method

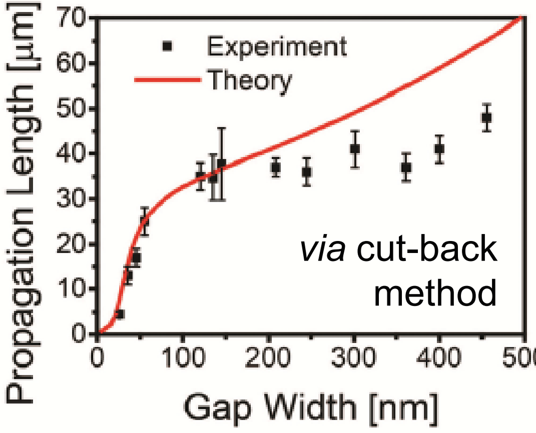
For characterization of SOI gap plasmon waveguides







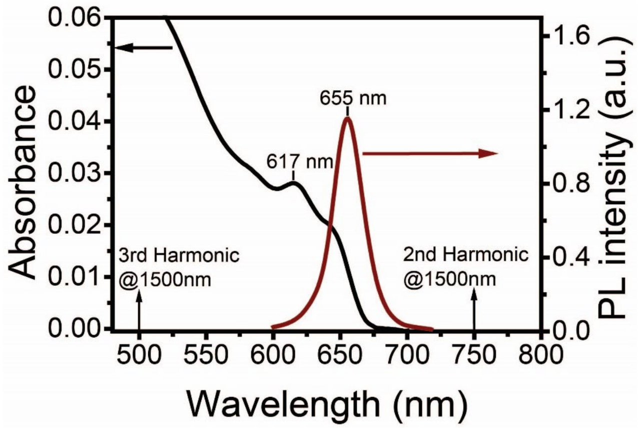


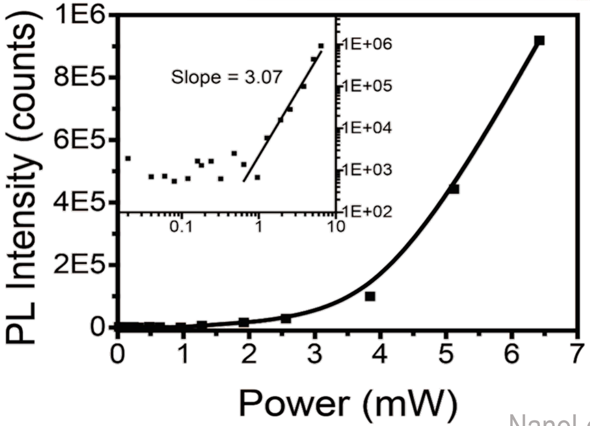


Cut-back method:

- ➢ Requires many sacrificial structures
- ➢ Measures propagation length
- ➢ Does not reveal mode location

Use selectively deposited SQDs!

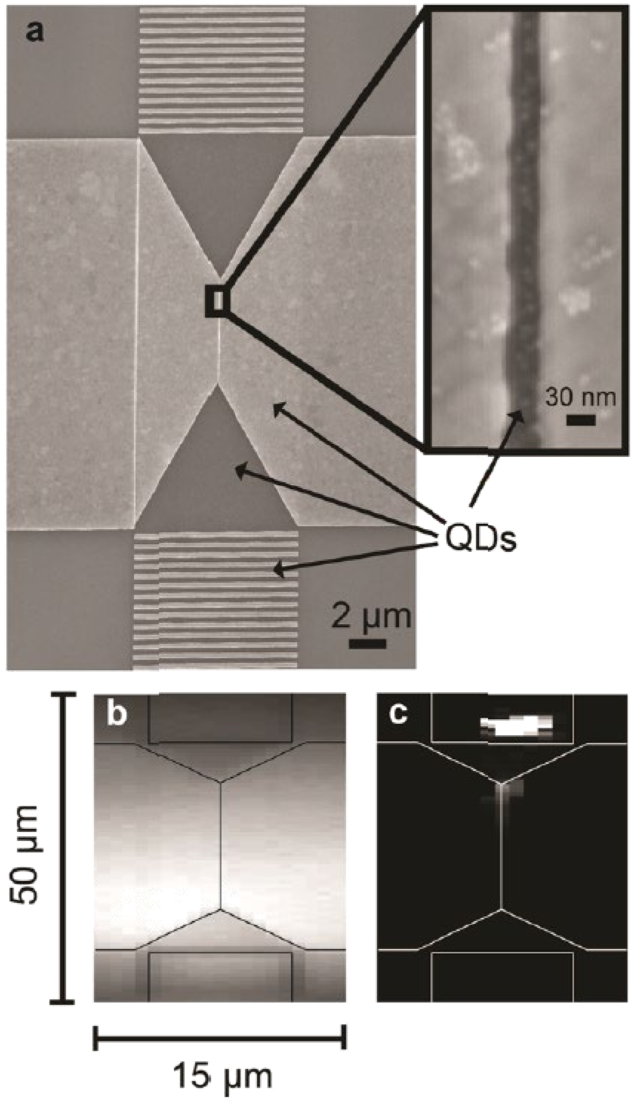




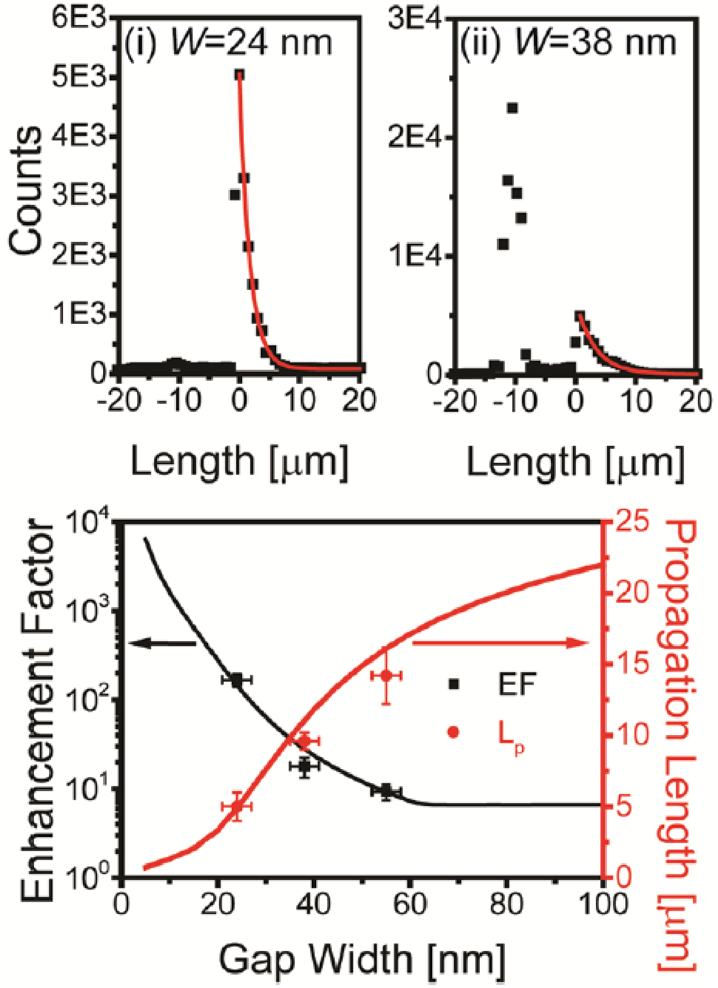
NanoLett **16**, 1410-1414 (2016)

Application of the 2-step EBL method

For characterization of SOI gap plasmon waveguides

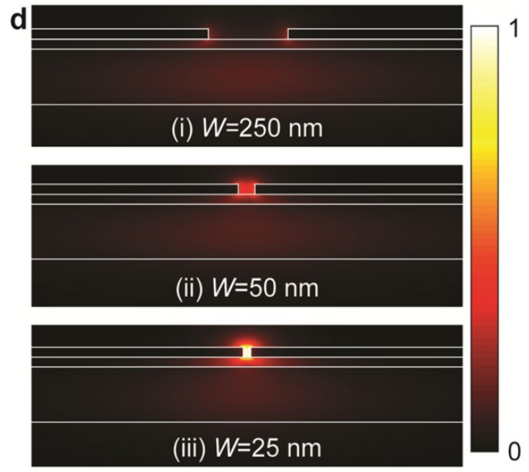


QDs' TPE mapping



Characterization of a single sacrificial structure:

- Direct measurement of propagation length from TPE data
- Direct confirmation of "nano-squeezing" of light



$$\mathrm{EF} = \left|\frac{I}{I_o}\right| = \frac{\left(\frac{C}{C_o}\frac{W_{\mathrm{pixel}}}{W}\right)^{1/3}\left(\frac{\rho_{\mathrm{QD}}(W)}{\rho_{\mathrm{QD}}(W_o)}\right)}{\eta_{\mathrm{grating}}}$$

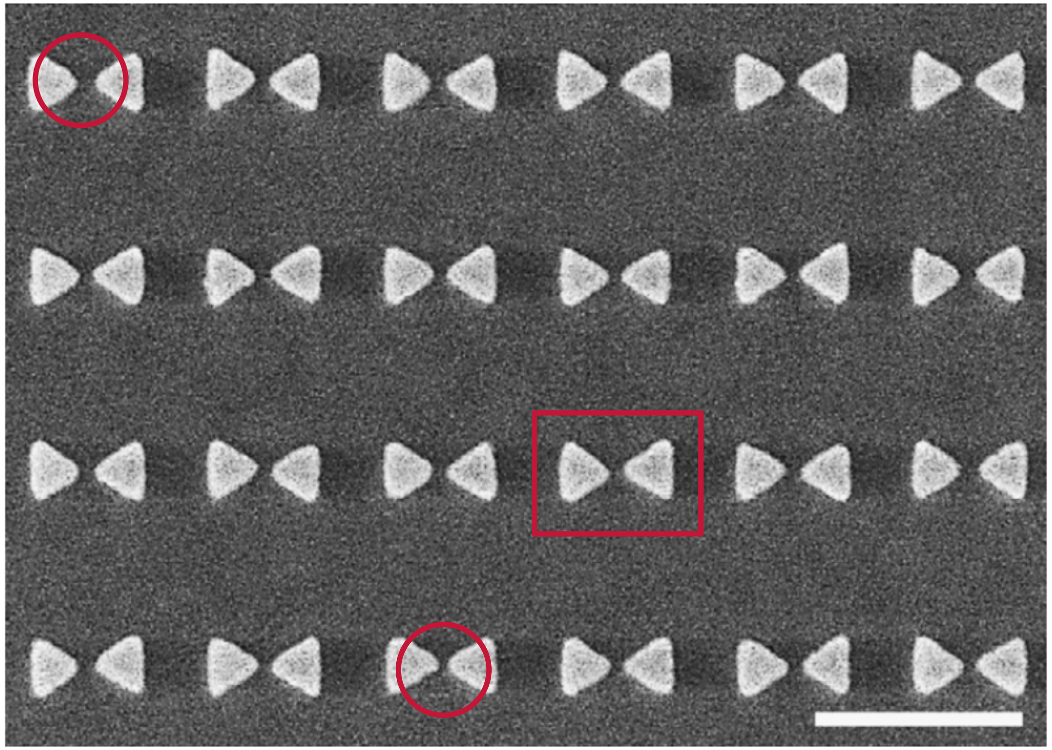
M.Nielsen et al. NanoLett **16**, 1410-1414 (2016)

Application of the 2-step EBL method

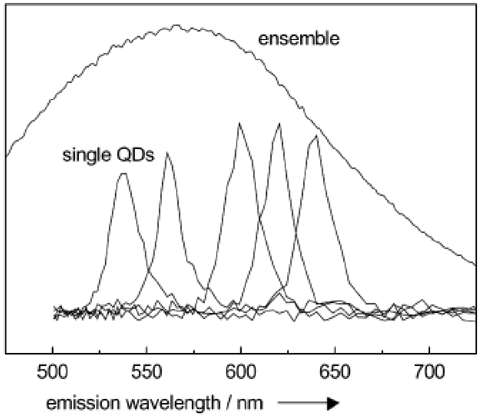
For deterministic control of radiative properties of QDs via exciton-plasmon coupling

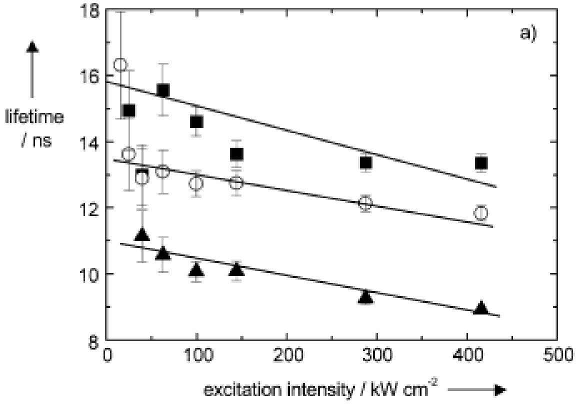
Plasmonic nanoantennas' performance depends on:
- Antenna shape & size
- Material from which it is made
- Dimension of gaps (if present)

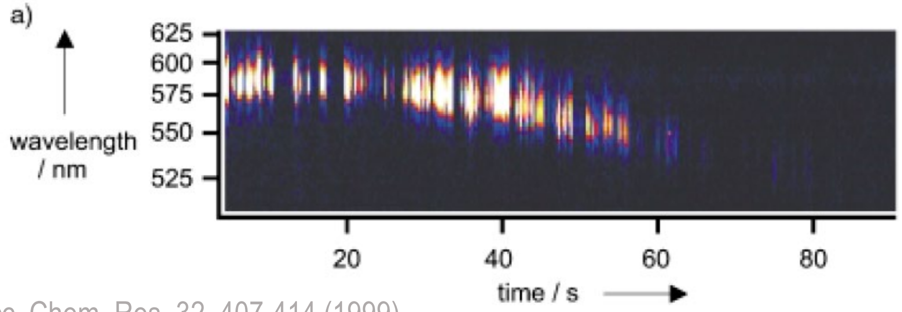
Colloidal QDs:
- Distribution of sizes (=λ_{em}) in a sample
- Blinking behaviour on a few/single QD level
- Blue-shifts and shortening of lifetime at high excitation intensities



Nature Comm. 5, 4427(2014)



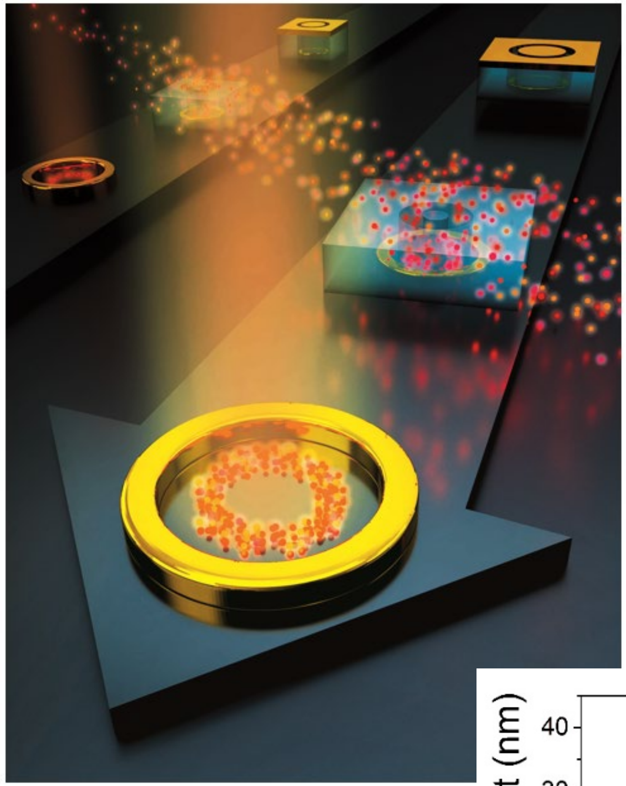




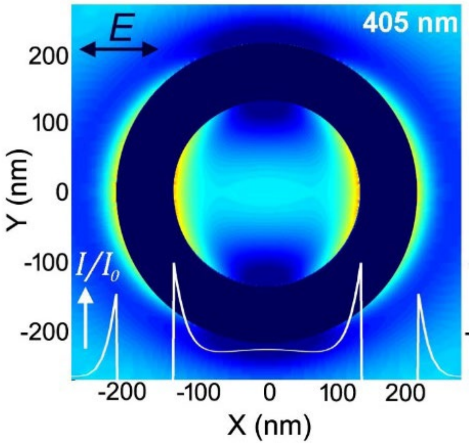
Acc. Chem. Res. 32, 407-414 (1999)
ChemPhysChem 3, 871-879 (2002)

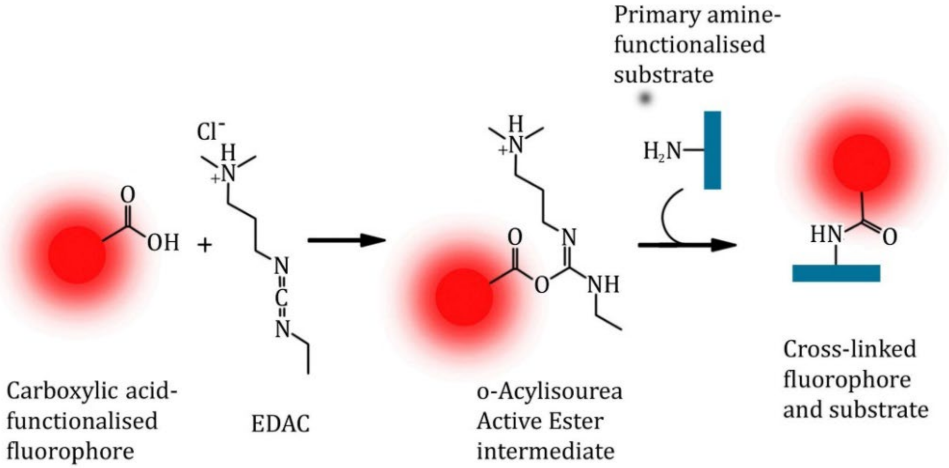
Application of the 2-step EBL method

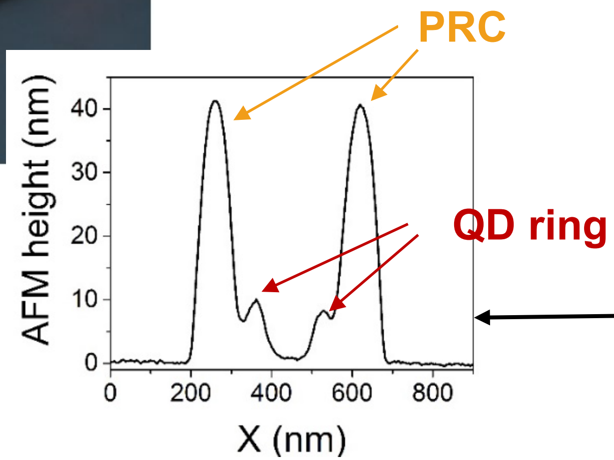
For deterministic control of radiative properties of QDs via exciton-plasmon coupling

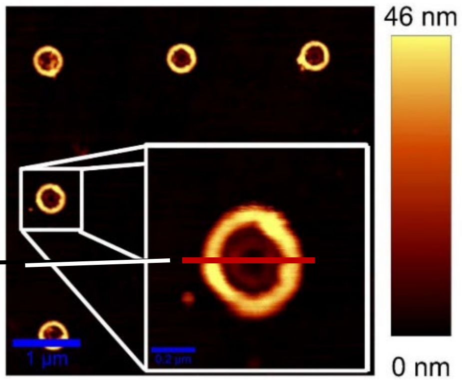


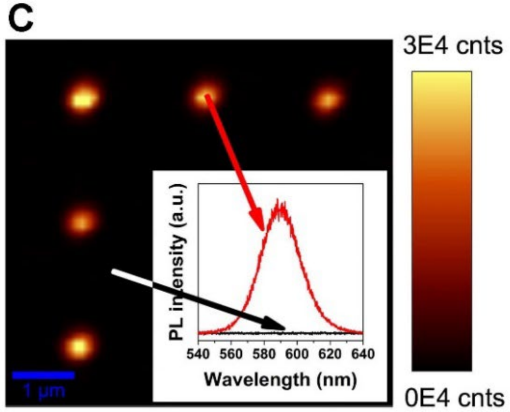
Selectively deposited colloidal QDs inside plasmonic ring cavities









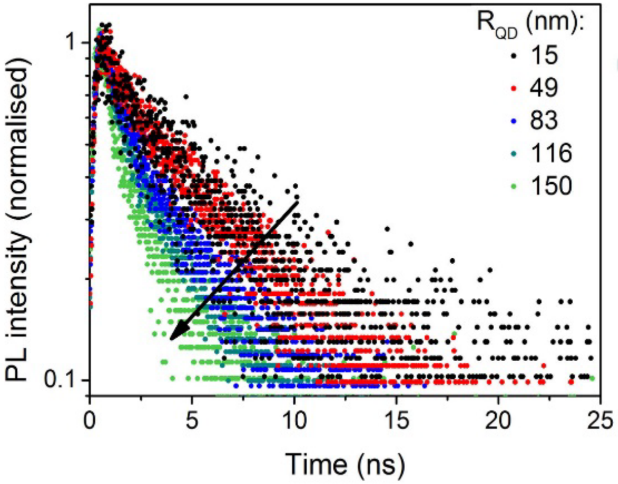


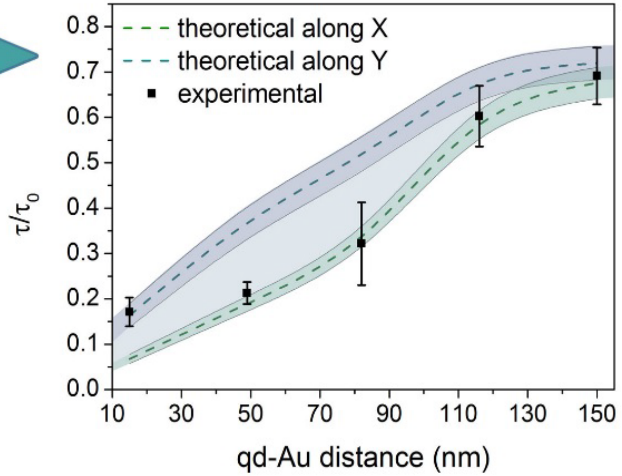
Application of the 2-step EBL method

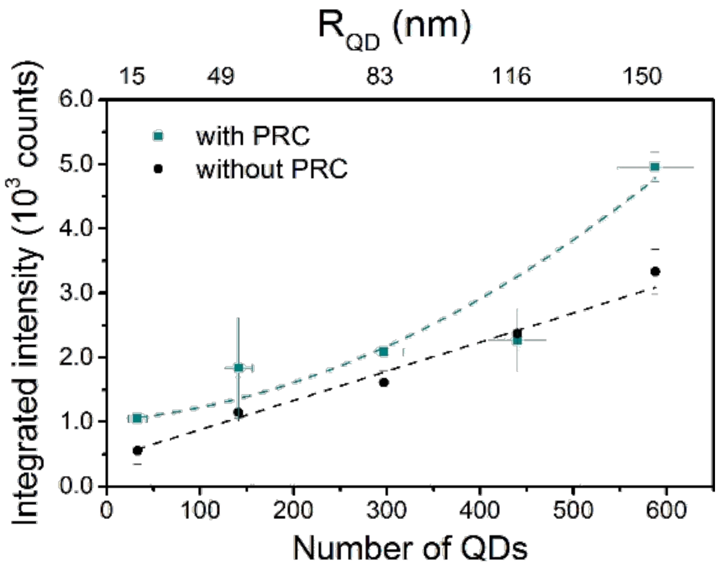
For deterministic control of radiative properties of QDs via exciton-plasmon coupling

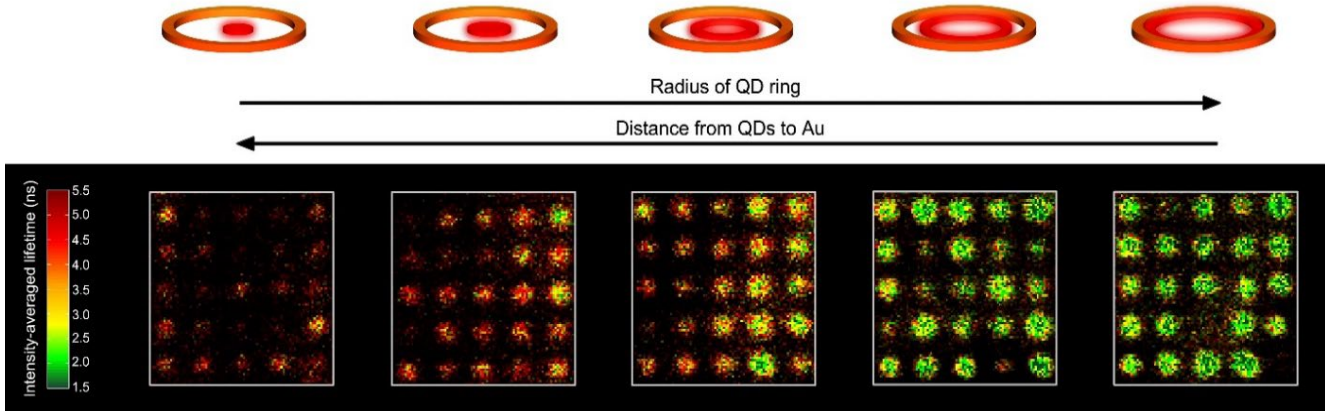
QD-PRC coupling

- Varied QD-PRC separation by increasing radius of QD ring
- Dimensions of PRC kept constant (D440t60)
- Strong change in radiative rates
- Good agreement with FDTD calculations







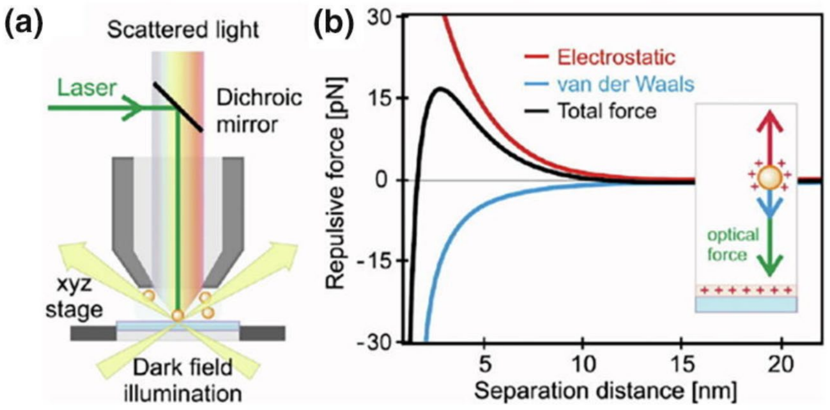


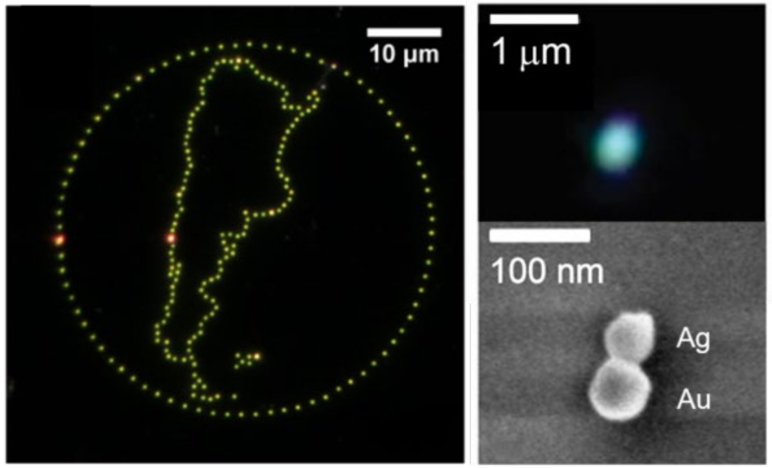
A. Rakovich et al. ACS Nano **9**, 2648-2658 (2015)

Going big!

Large-area printing & deposition techniques

Optical printing of metallic NPs

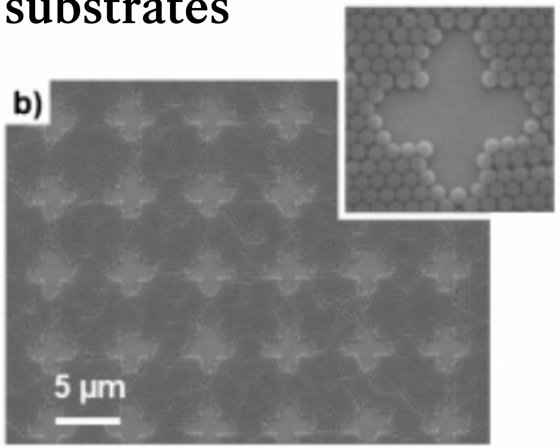


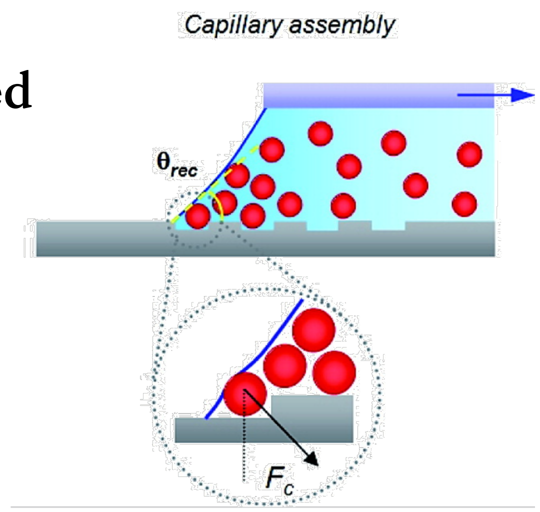


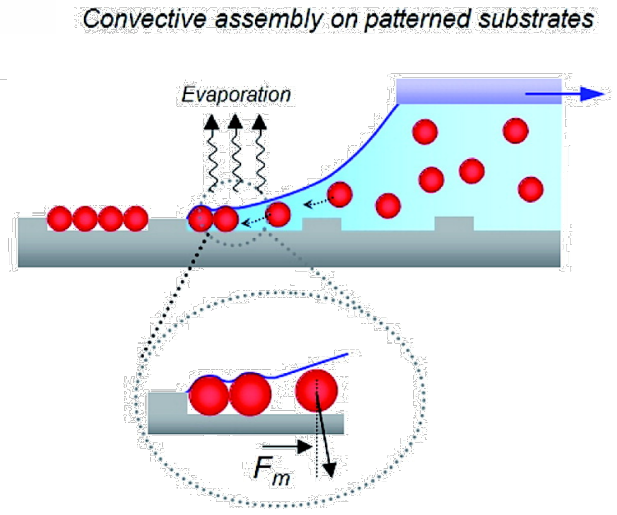
Linhan Lin et al. Materials Today 28, 49-62 (2019)

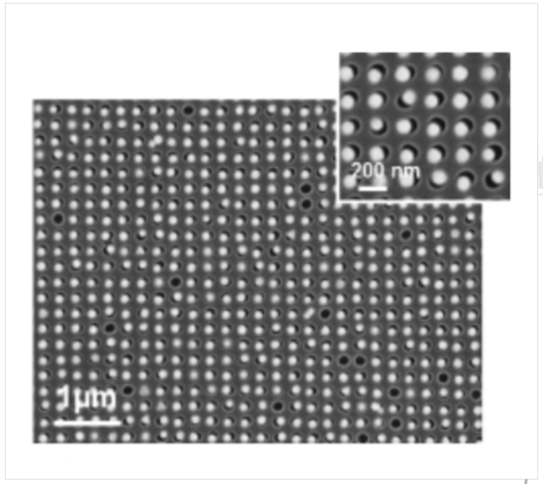
Julian Gargiulo et al. NanoLetters 16, 1224-1229 (2016)

Capillary and convective assembly on pre-patterned substrates







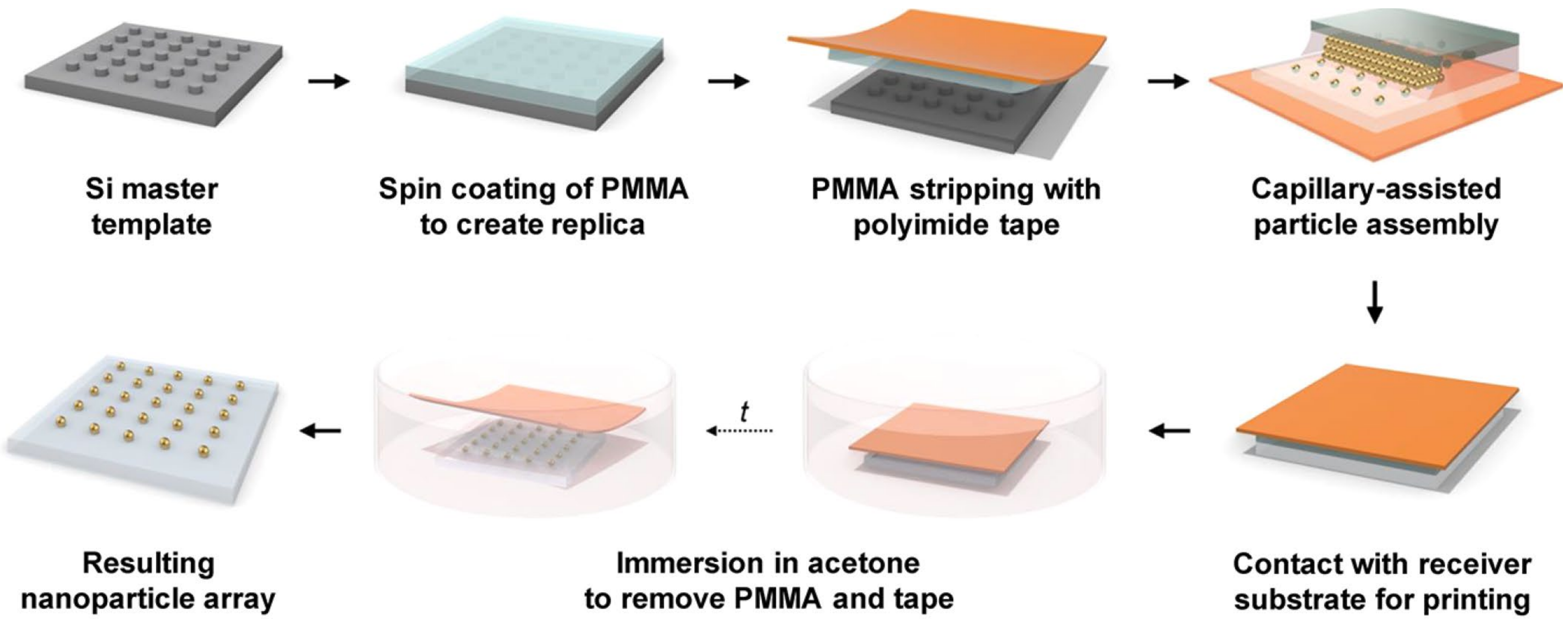


L. Malaquin et al., Langmuir 23, 11513 (2007)

Introduction
Self-assembly
Nano-bio hybrids
Superclusters
Localization
2-step EBL
Template dissolution
Active control
Brownian ratchets
Conclusions

Large-area immobilization of Au NPs arrays

CAPA (Capillary assisted particle assembly) + Stamping + Template-dissolution



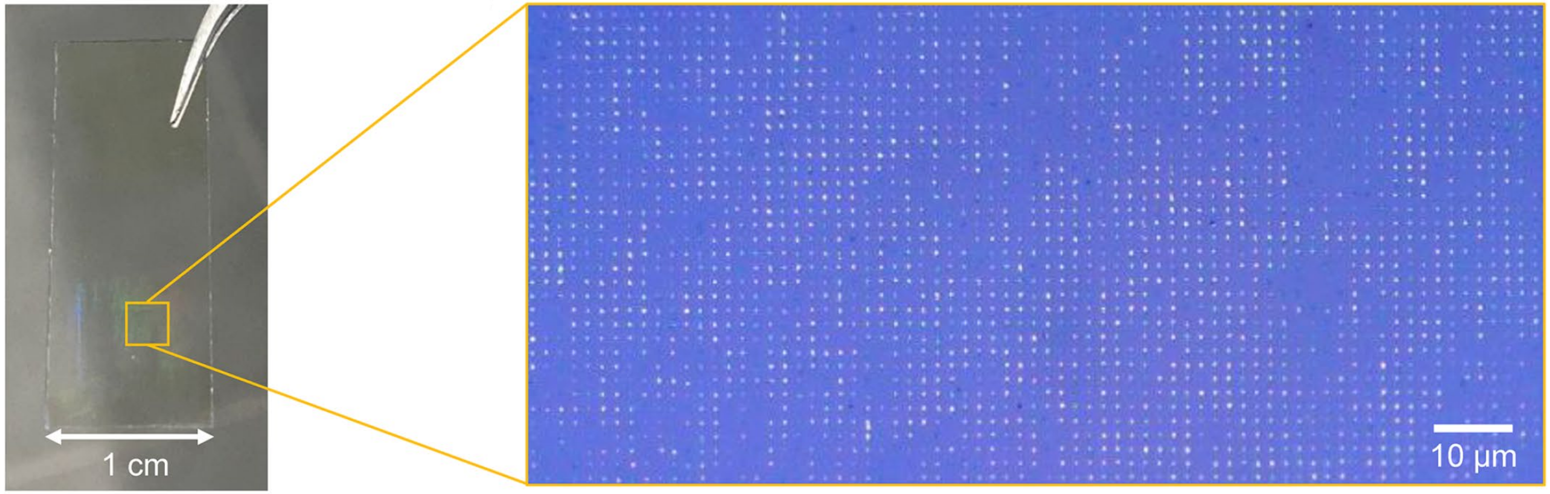
In collaboration with LMU, ICL, KAIST, SUST

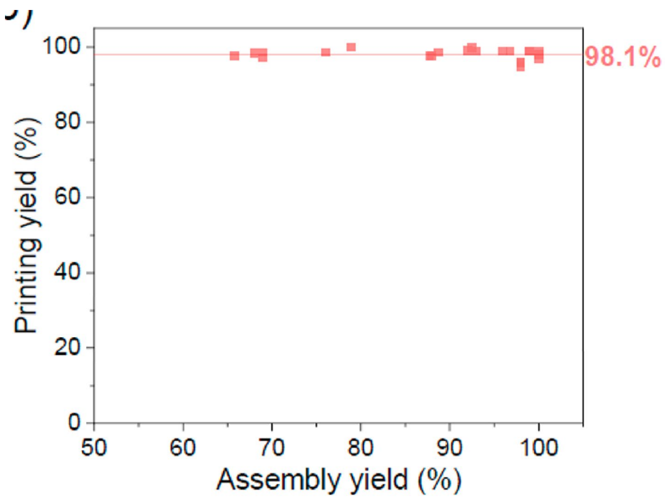
J.B. Lee et al., ACS Nano 2020, 14, 17693

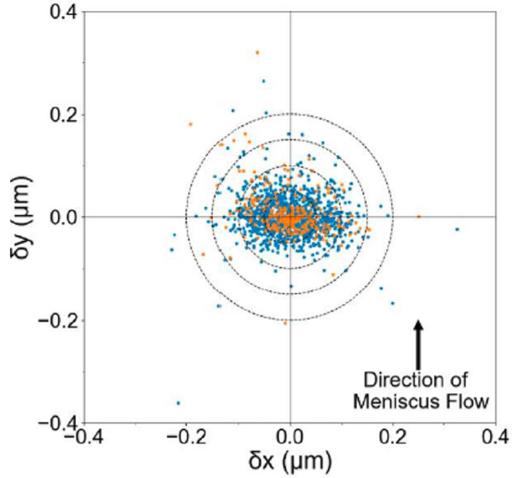
Introduction
Self-assembly
Nano-bio hybrids
Superclusters
Localization
2-step EBL
Template dissolution
Active control
Brownian ratchets
Conclusions

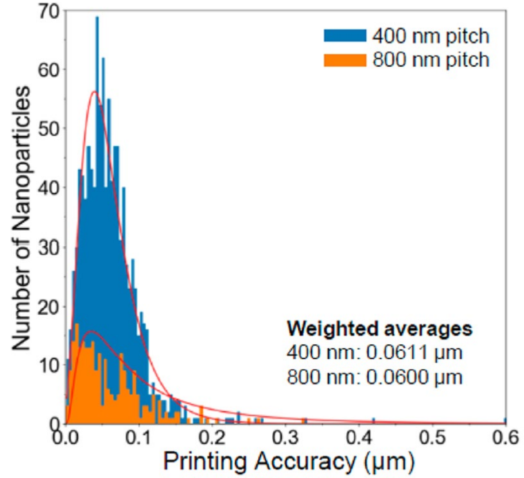
Large-area immobilization of Au NPs arrays

Printing accuracy and yield









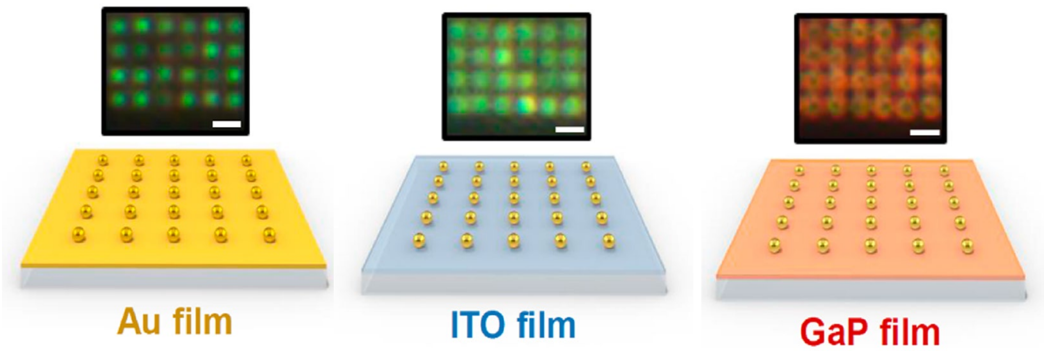
In collaboration with LMU, ICL, KAIST, SUST

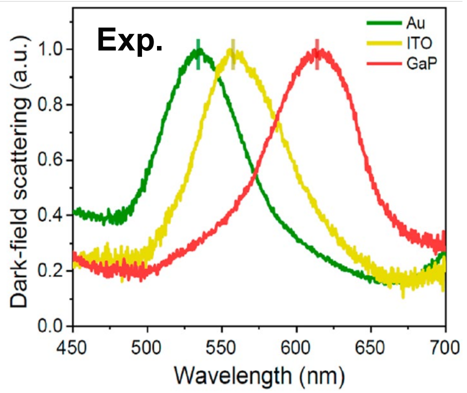
J.B. Lee et al., ACS Nano 2020, 14, 17693

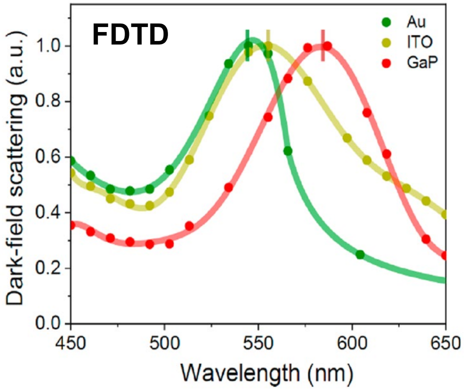
Large-area immobilization of Au NPs arrays

Printing on different substrates

- Assembly conditions depend on NP and substrate type
- Works for any substrate not soluble in acetone
- Can be used with pre-existing structures

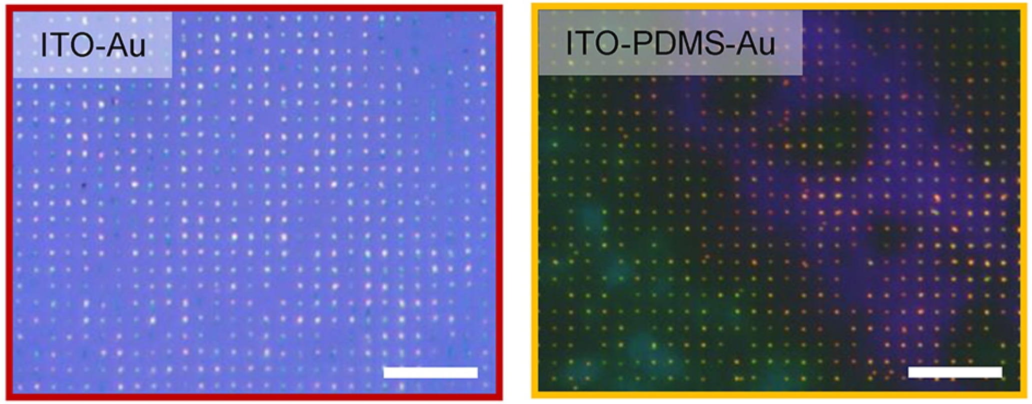


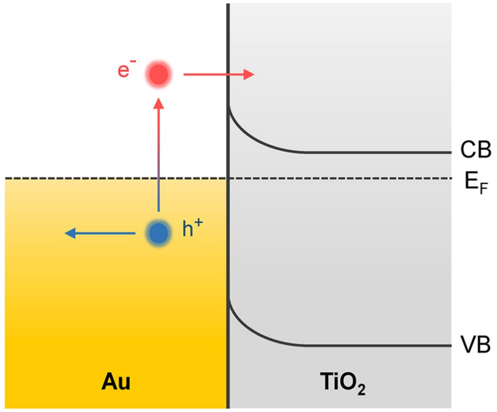


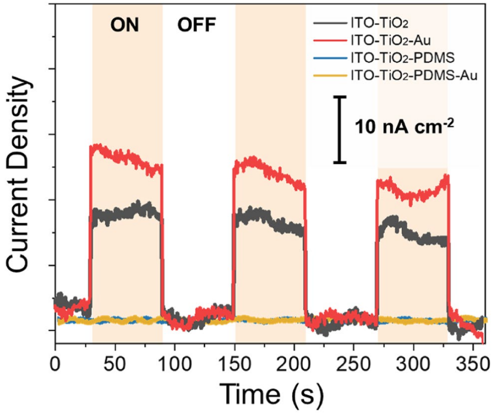


Hot-electron detection

via an introduction of a tunnelling junction







In collaboration with LMU, ICL, KAIST, SUST

J.B. Lee et al., ACS Nano 2020, 14, 17693

Active control of colloidal nanoparticles

In aqueous environments

Active control can enable

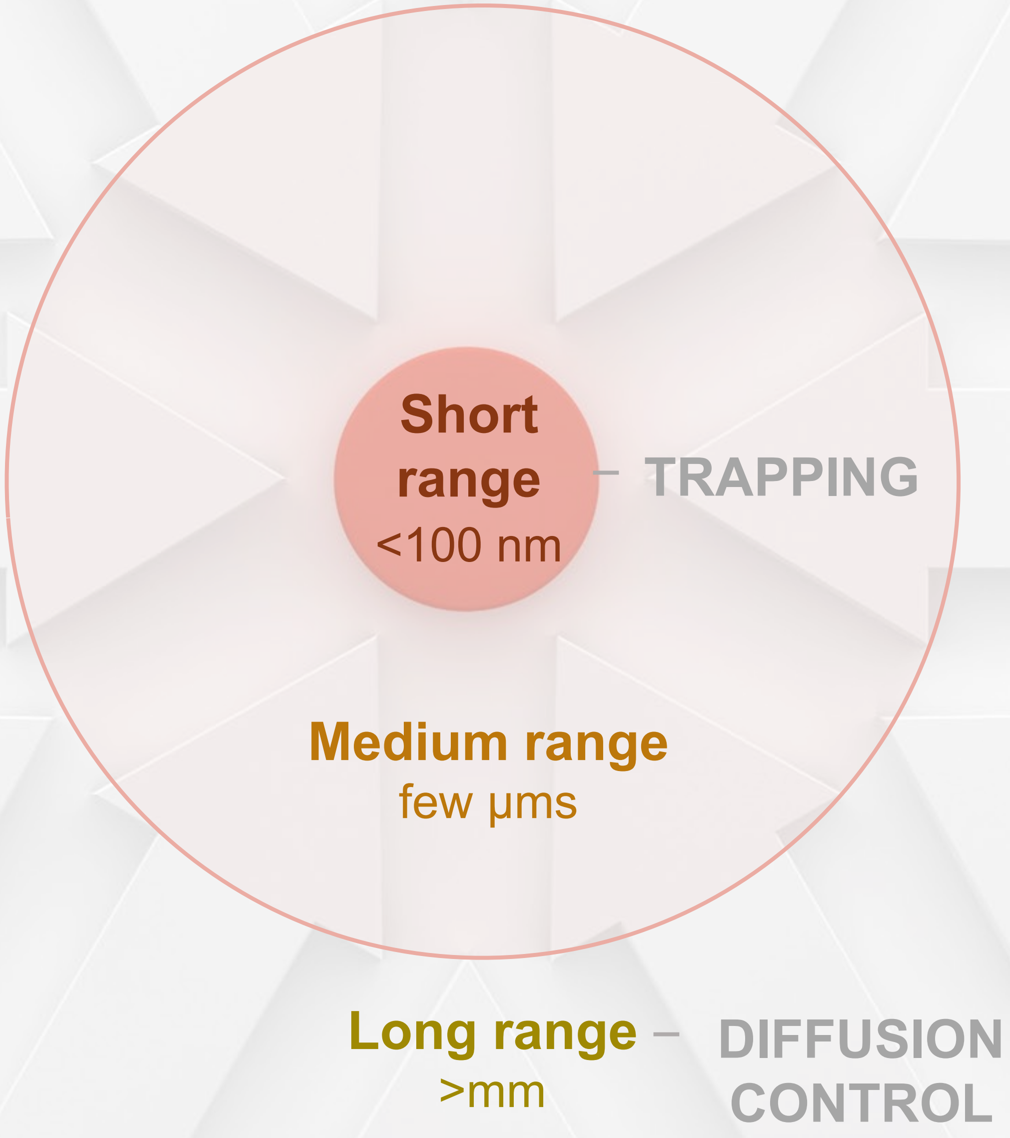
- Particle sorting
- Temporary/permanent concentration of samples
- Delivery of test materials to sensing areas

Allowing

- Lower LODs in sensing schemes
- In-situ measurements ranging from on single-particle level to ensemble level on same sample

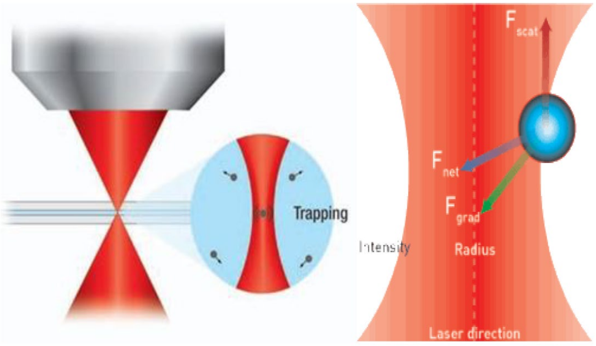
Various forces can be utilized

- Have different action ranges

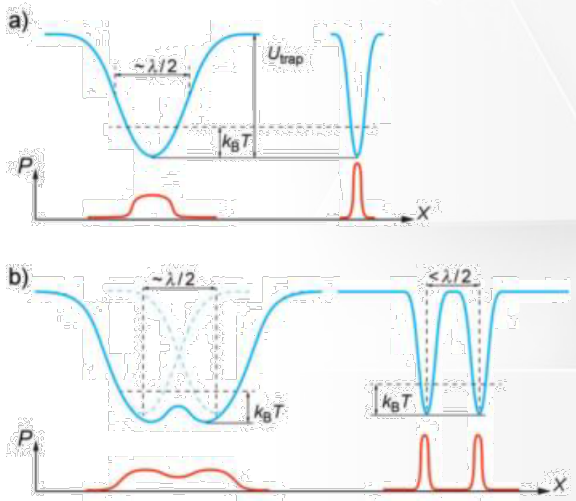


Active control of colloidal nanoparticles

Optical trapping
(Usually) short range



Ashkin, (1986)

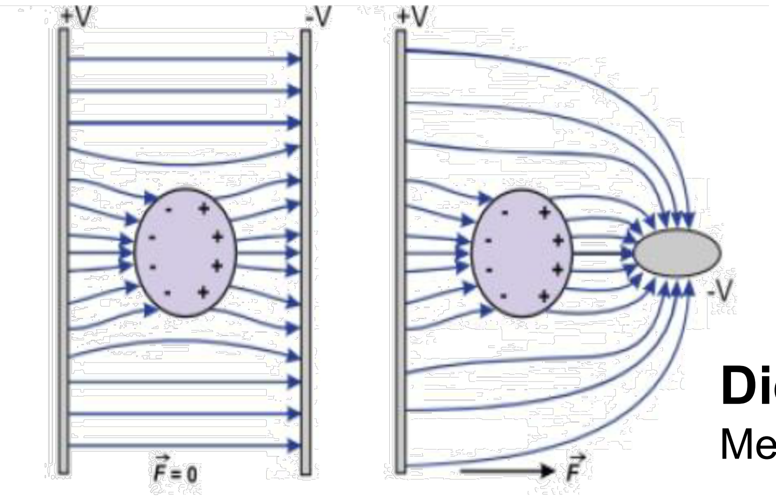


Wang et al., ChemPhysChem 13, 2639 (2012)

Short range
<100 nm – **TRAPPING**

Medium range
few µms

Long range – **DIFFUSION CONTROL**
>mm



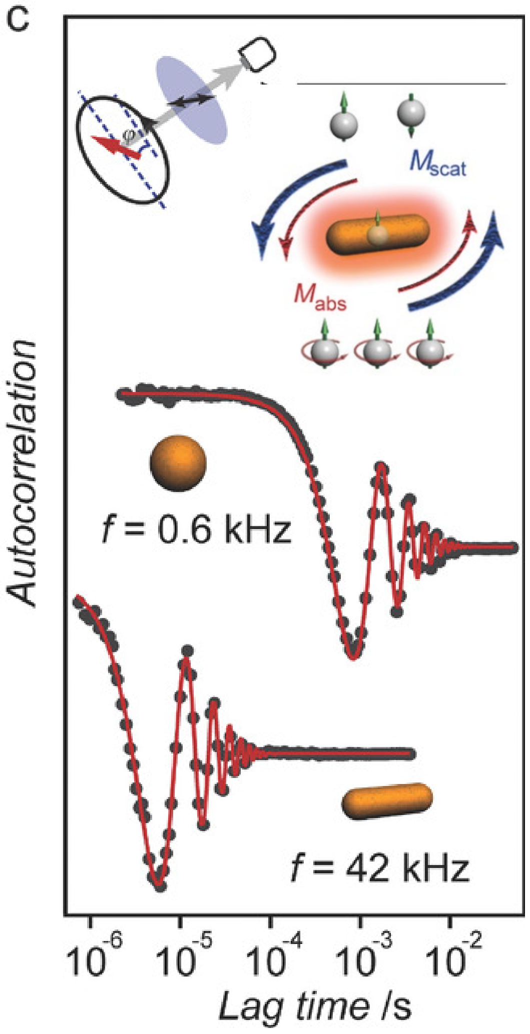
Dielectrophoresis
Medium-to-long range

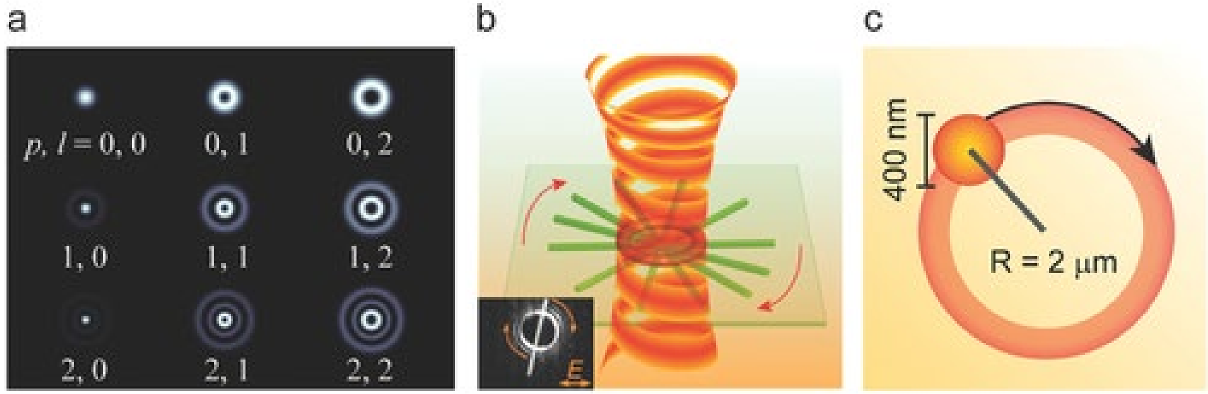
Electrophoresis, 32 2307 (2011)

Introduction
Self-assembly
Nano-bio hybrids
Superclusters
Localization
2-step EBL
Template dissolution
Active control
Brownian ratchets
Conclusions

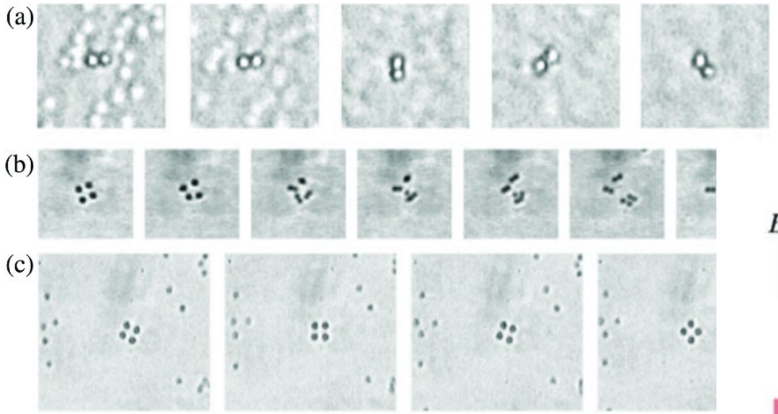
Control of nanoparticle motion in solution using SLMs

doi.org/10.1002/adfm.201706272

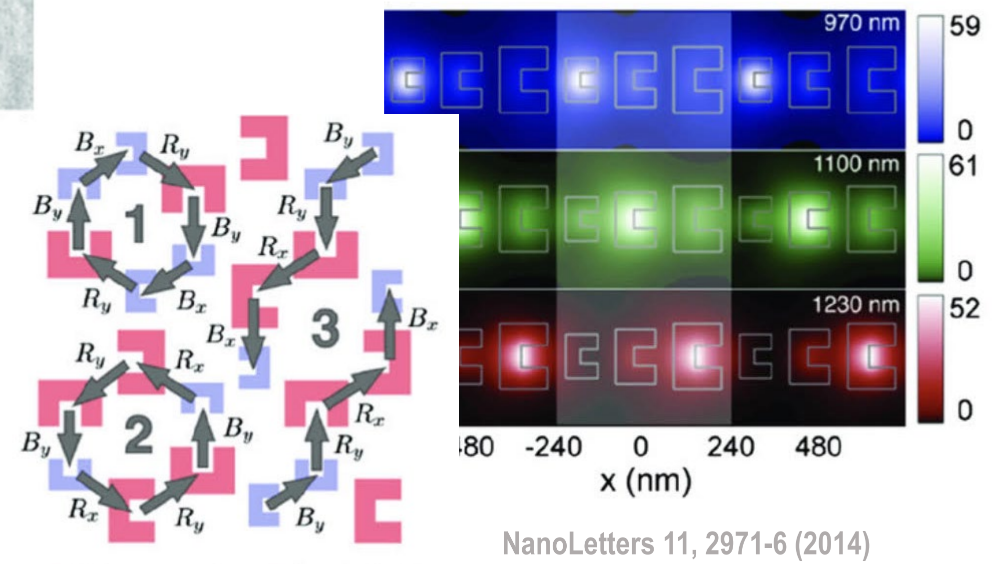




J. Phys. Chem. Lett. 2013, 4, 17, 2937–2942



Science, 296 (5570), 1101 –1103 (2002)



modulating wavelength / polarization

NanoLetters 11, 2971-6 (2014)

Active control of colloidal nanoparticles

In aqueous environments

Active control can enable

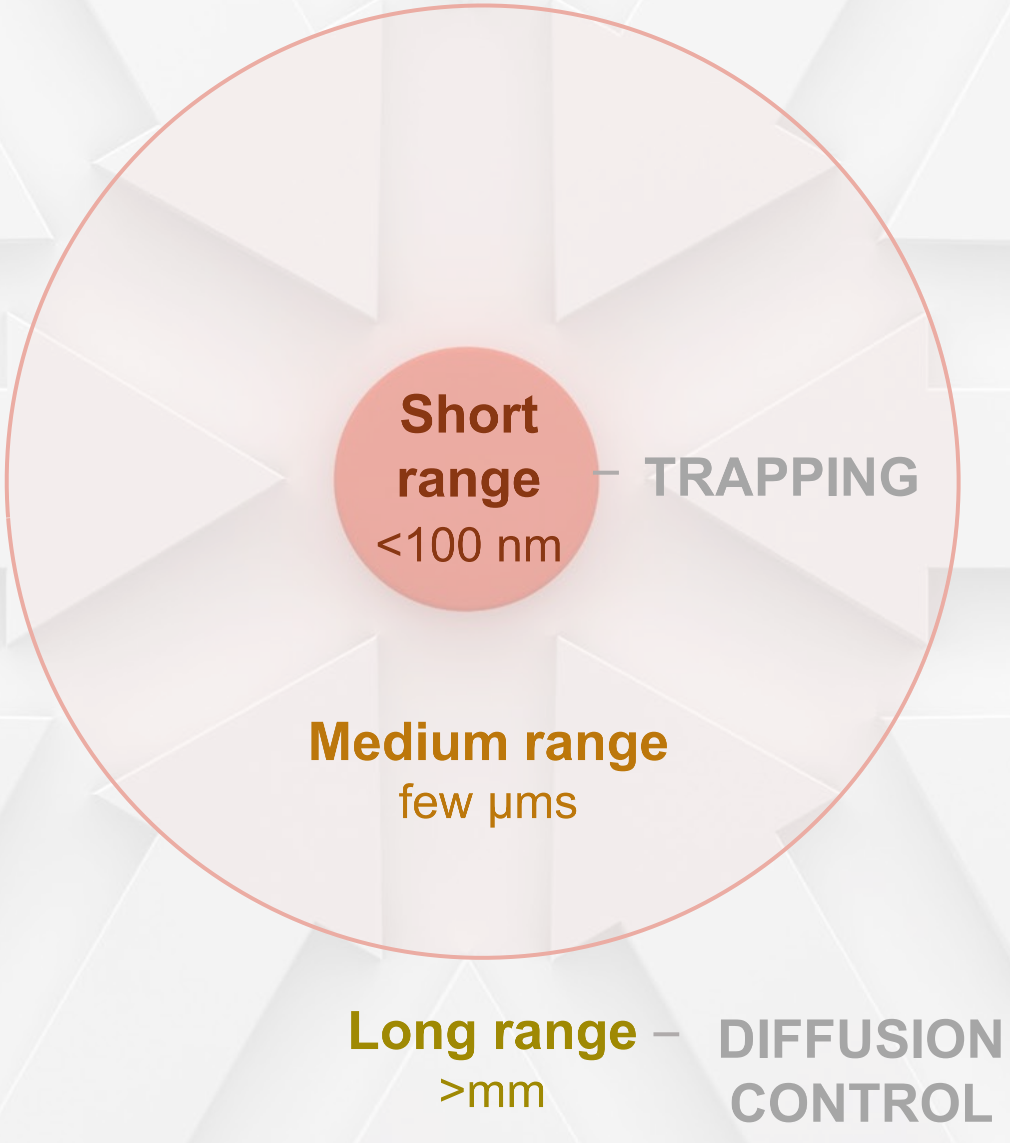
- Particle sorting
- Temporary/permanent concentration of samples
- Delivery of test materials to sensing areas

Allowing

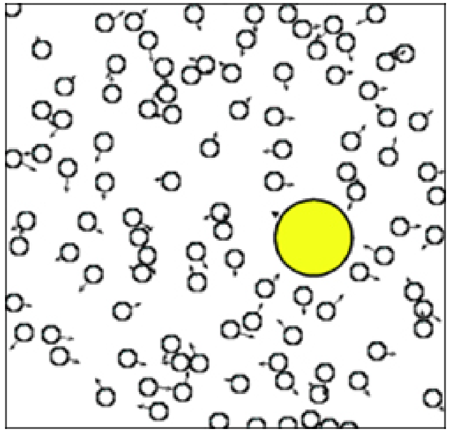
- Lower LODs in sensing schemes
- In-situ measurements ranging from on single-particle level to ensemble level on same sample

Various forces can be utilized

- Have different action ranges



Brownian motion of particles in solutions



Brownian motion

- ➢ Stochastic process resulting in random motion
- ➢ Mean Square displacement for an ensemble:

$$\langle (x_t - x_0)^2 \rangle = 2Dt$$

where D is the diffusion coefficient:

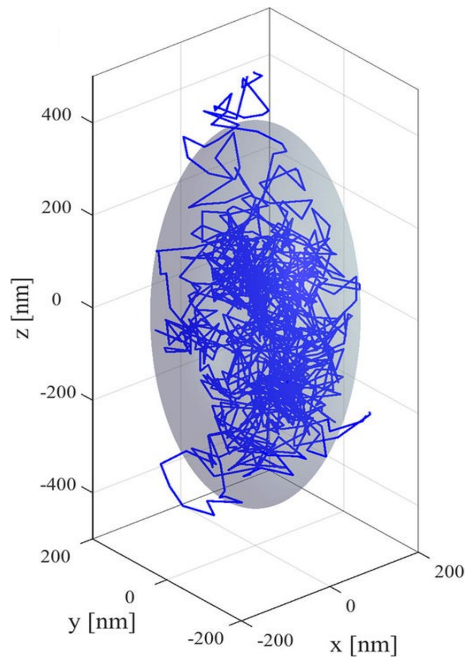
$$D = \frac{k_B T}{\gamma}, \quad \gamma = 6\pi\eta a$$

Particle diffusion in presence of a potential

- ➢ Additional forces are exerted on particles
- ➢ Brownian motion “adds” thermal noise

Can exploit this noise for long range transport!

Particle motion in an optical trap

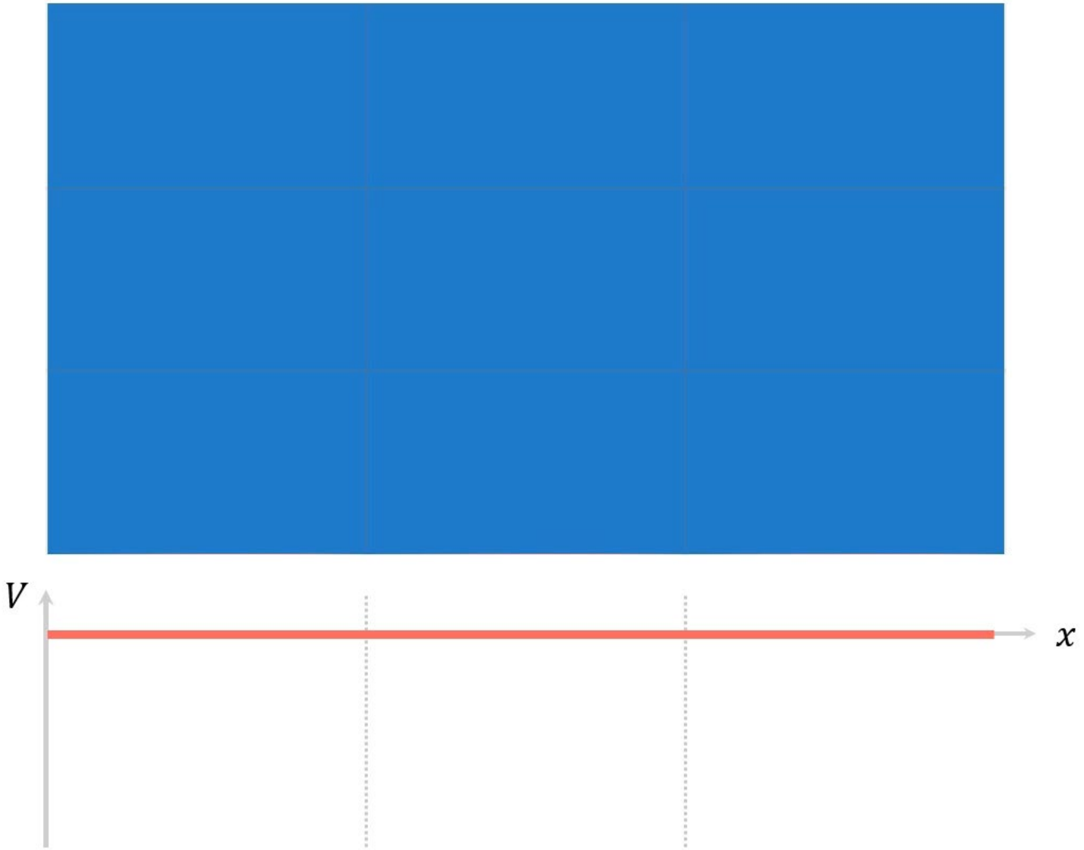


Eur. Phys. J. Plus 135, 949 (2020)

Rectification of Brownian motion

Through application of period & asymmetric potential

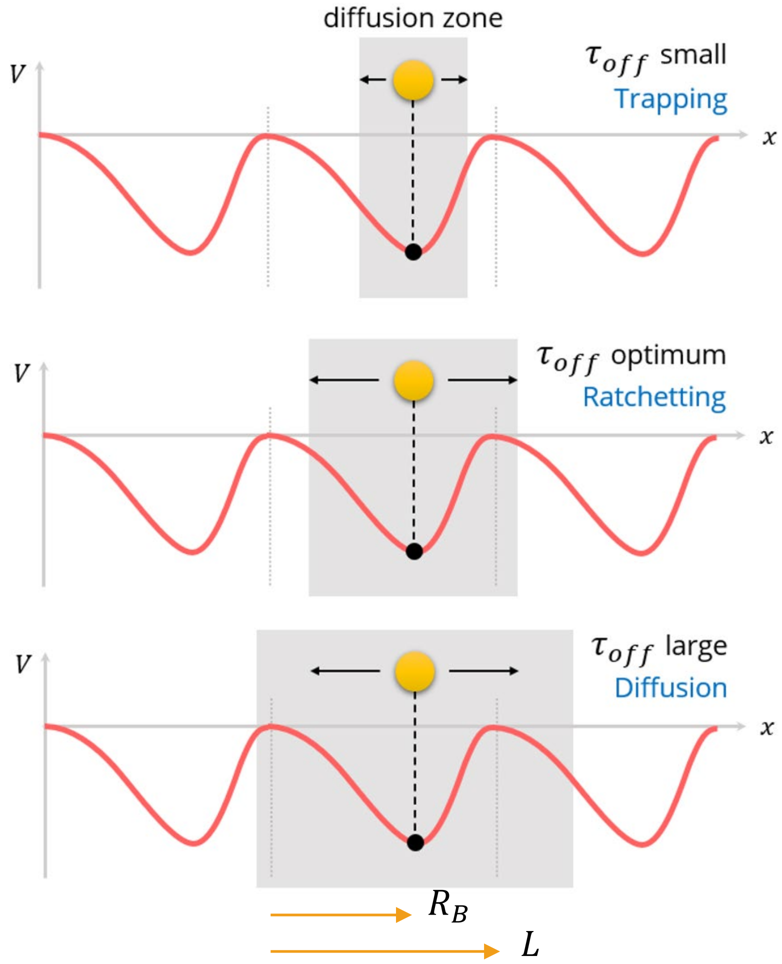
LASER: OFF



Can use any type of potential as long as it is switchable

Optimum time to keep the potential off:

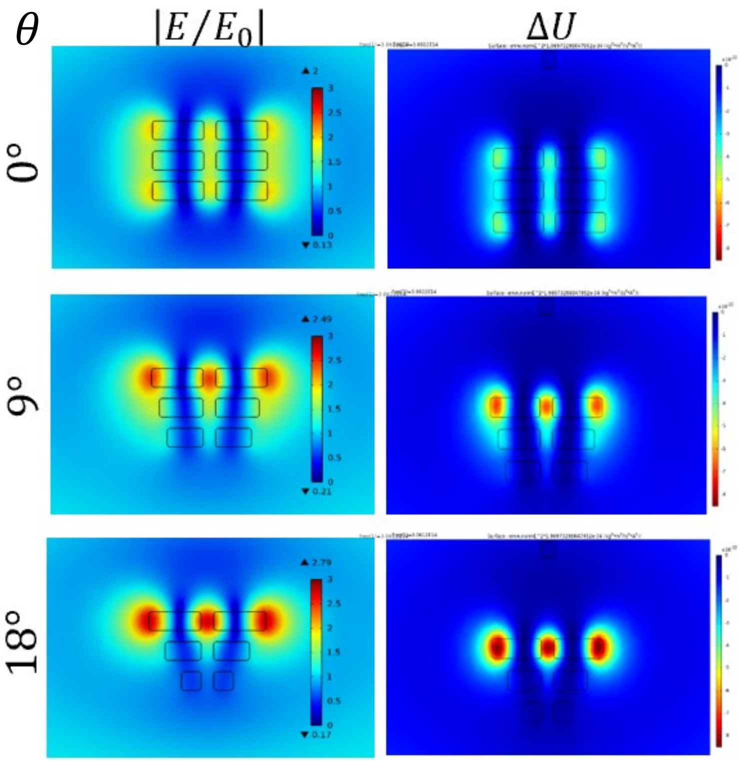
$$\tau_F = \frac{(L-R_B)^2}{2D} < \tau_{off} < \tau_B = \frac{R_B^2}{2D}$$



Plasmonic Brownian ratchets

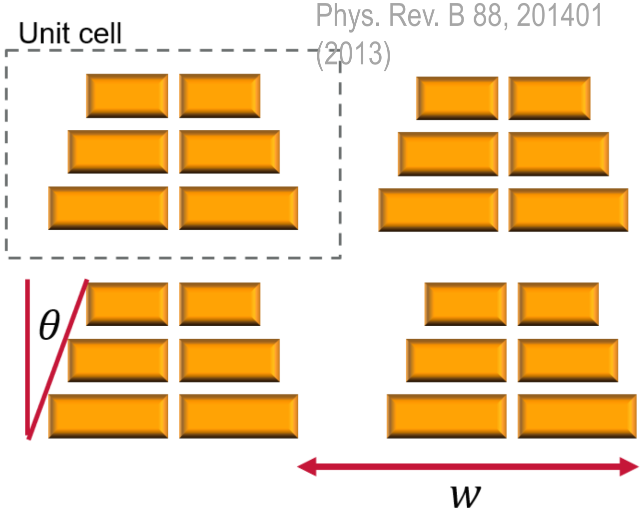
Advantages

- Easily designed / fabricated
- Asymmetries easy to implement
- Reduced power requirements
- Simple implementation

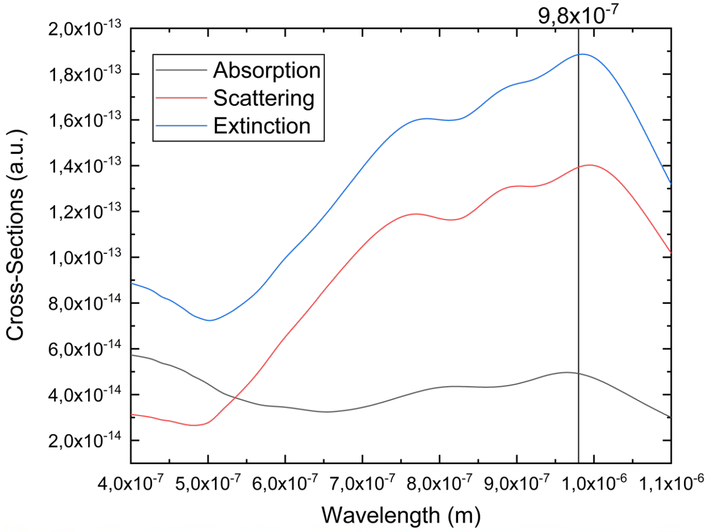


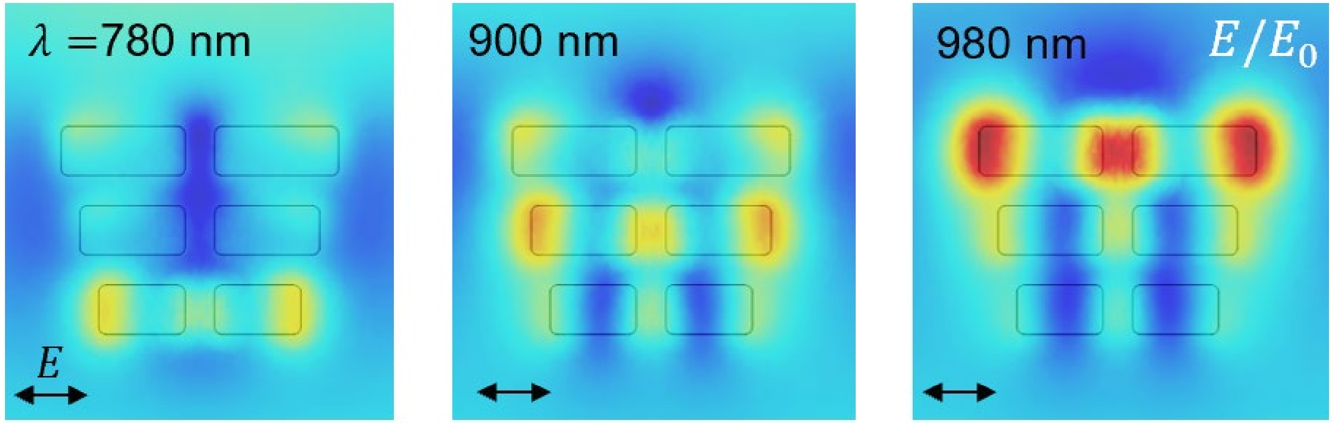
Ratchet design

- Strong resonance at target λ
- Asymmetric potential profile



Phys. Rev. B 88, 201401 (2013)

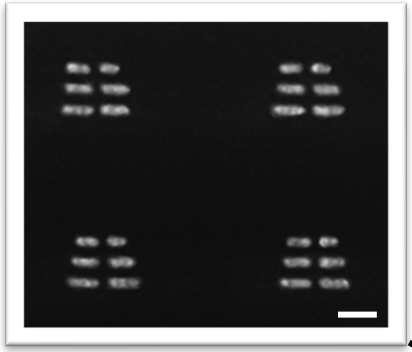


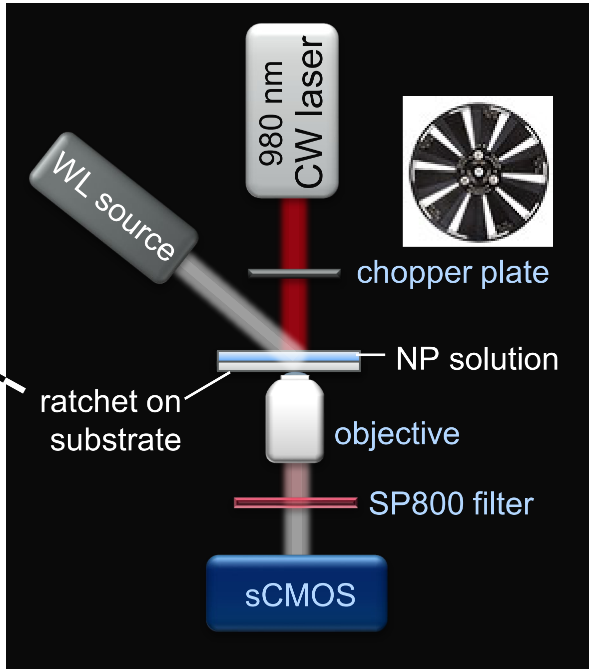


In preparation

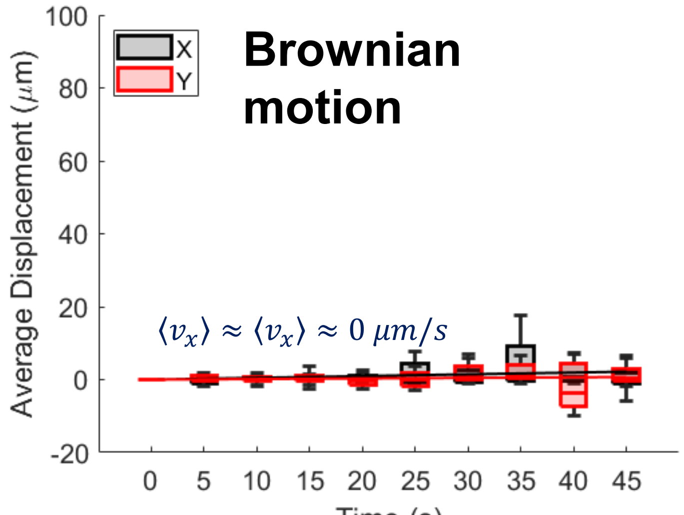
Experimental implementation of plasmonic Brownian ratchets

- Chopped 980 nm CW excitation
- Max power used 2.5 kW/cm^2
- Chopping: 50/50 duty cycle
- Adjustable frequency
- Aqueous solutions of various NPs

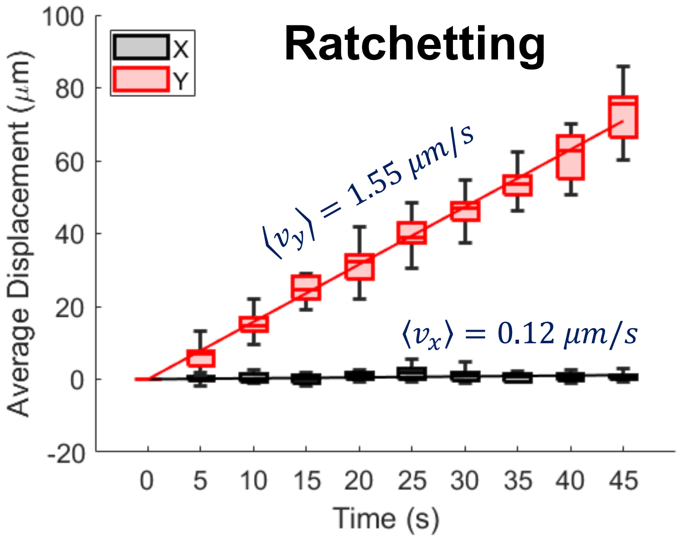


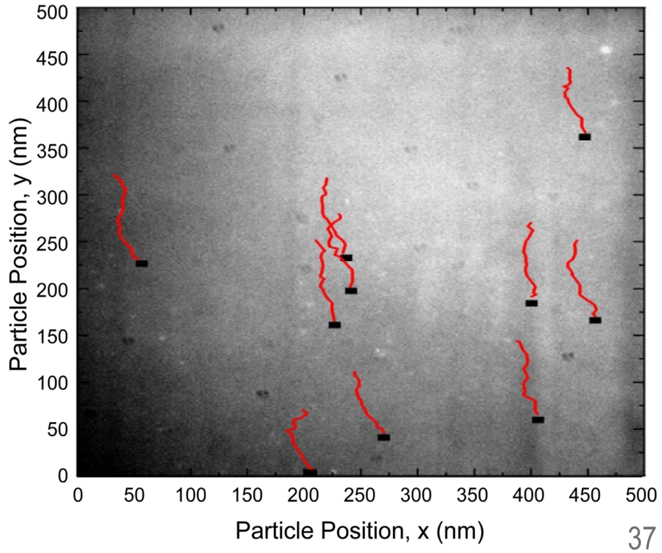


	Polystyrene (40 nm)	Polystyrene (200 nm)	PTB7 (180 nm)
$\langle v_x \rangle$	0.14 μm/s	0.12 μm/s	0.15 μm/s
$\langle v_y \rangle$	2.37 μm/s	1.55 μm/s	1.84 μm/s



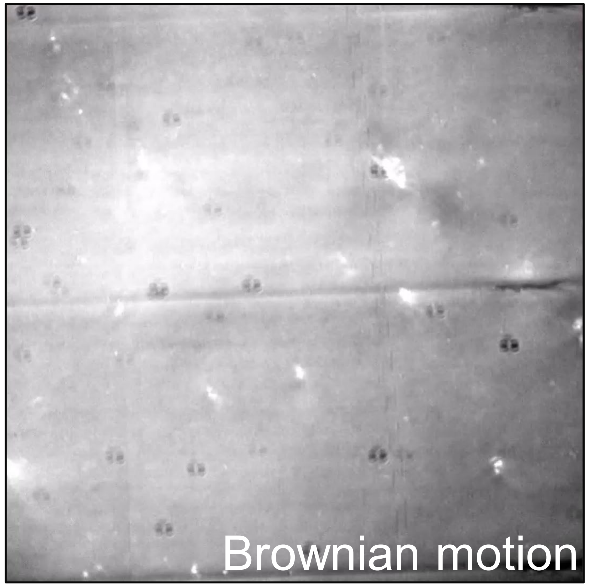
In preparation

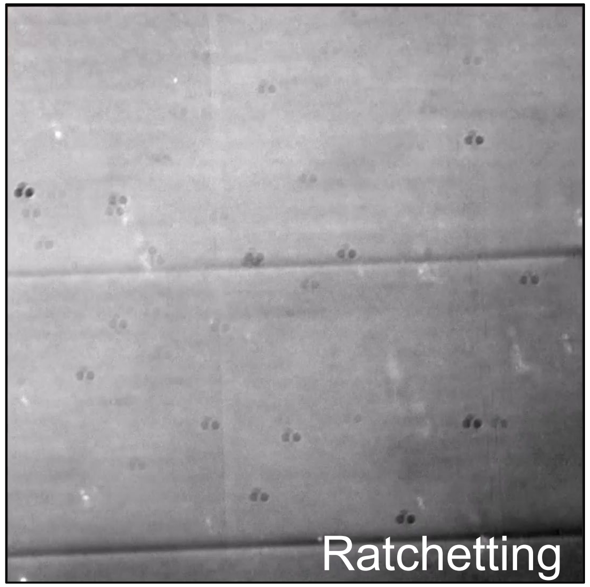


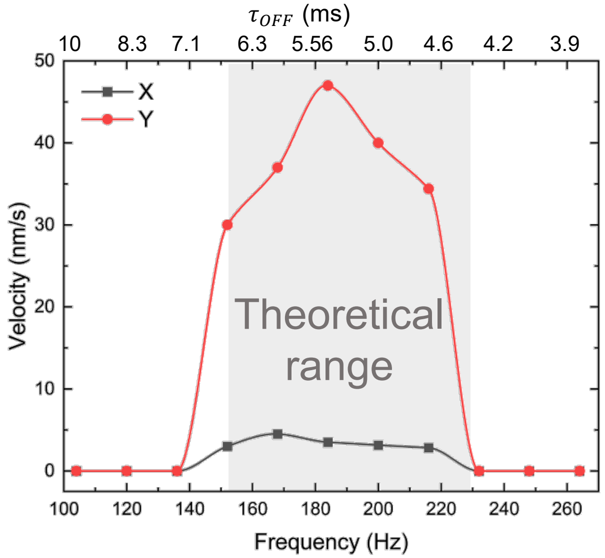


Experimental implementation of plasmonic Brownian ratchets

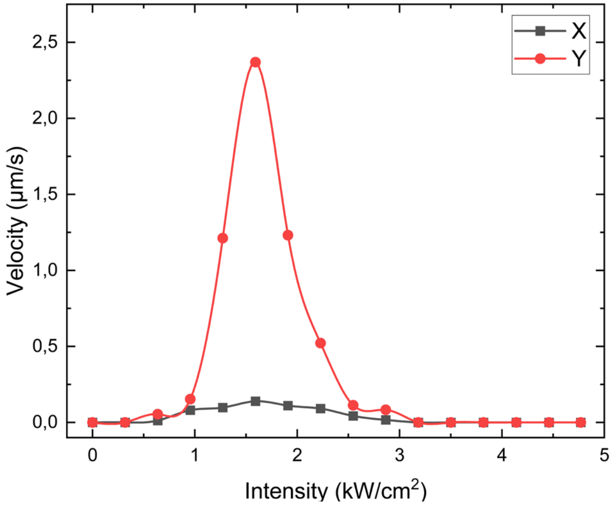
Polystyrene spheres, 40 nm diameter





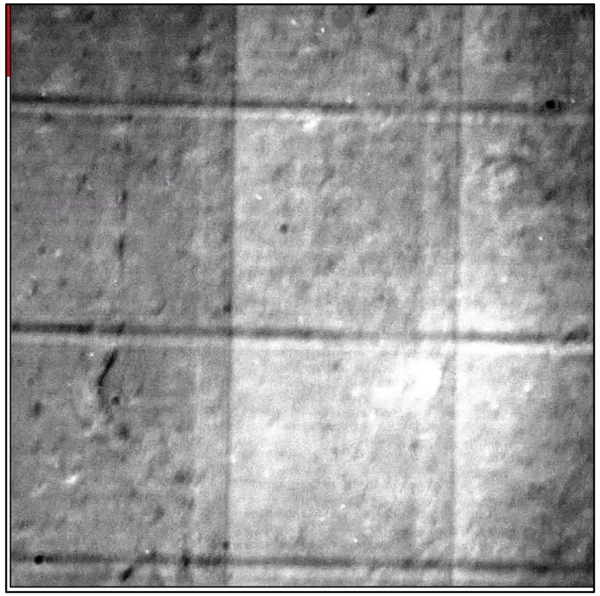


In preparation

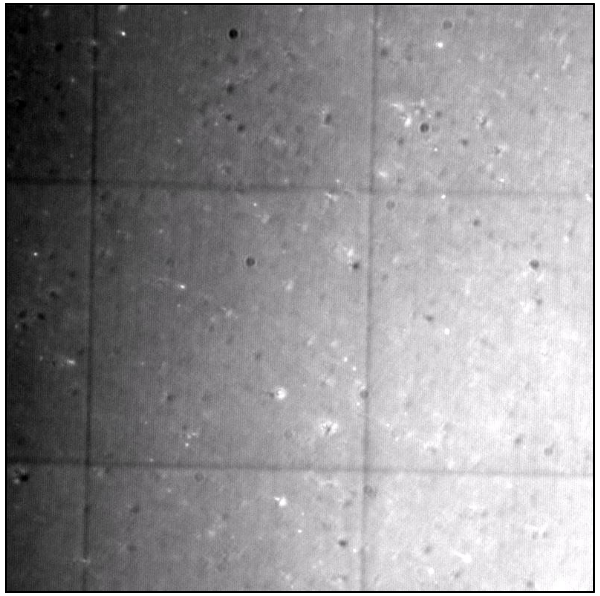


Other sizes/materials

PS spheres, 200 nm



PTB7 CPNs, 180 nm



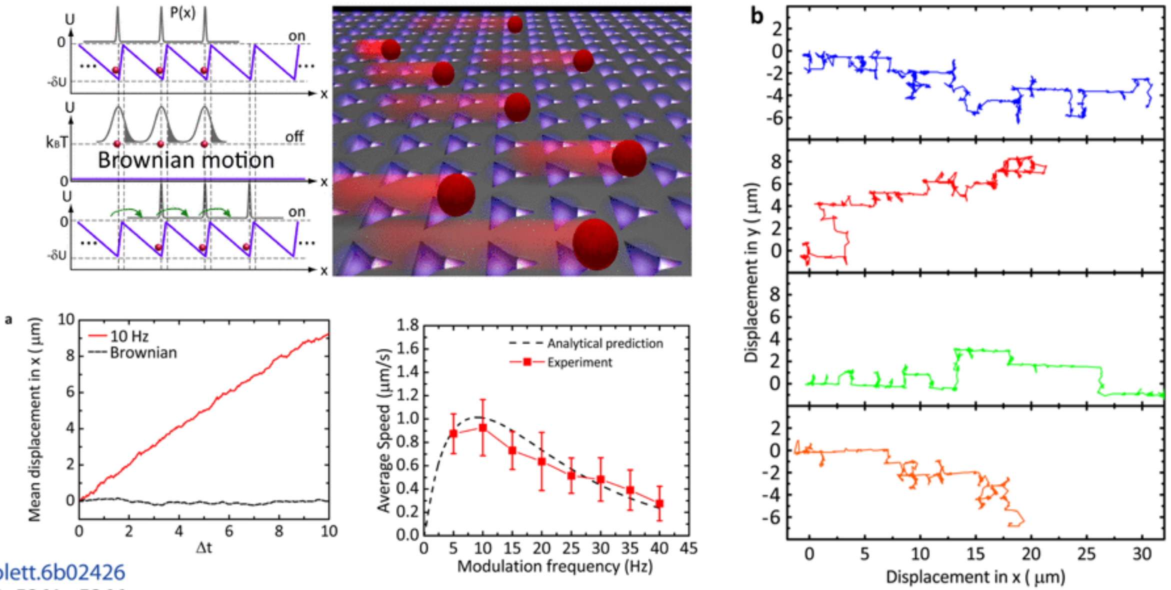
Comparison to other optically-driven Brownian ratchets

Optical ratchets

Near-Field, On-Chip Optical Brownian Ratchets

Shao-Hua Wu, Ningfeng Huang, Eric Jaquay, and Michelle L. Povinelli*

Ming Hsieh Department of Electrical Engineering, Viterbi School of Engineering, University of Southern California, Los Angeles, California 90089, United States



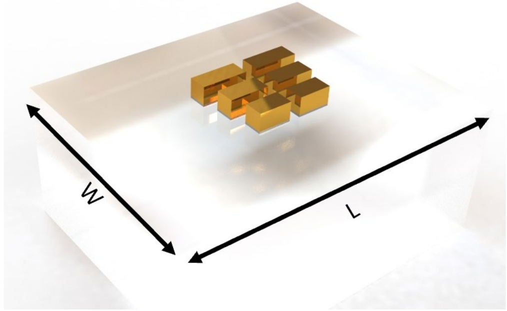
DOI: 10.1021/acs.nanolett.6b02426
Nano Lett. 2016, 16, 5261−5266

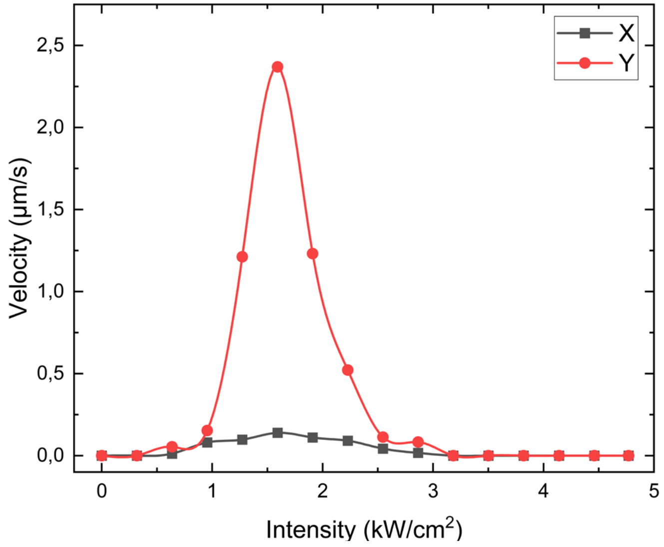
Average speed = 1 μm/s

Coupled power = 100 μW/μm² = 10⁸ W/m²

Analyte = ⌀520 nm polystyrene spheres

Our plasmonic ratchets





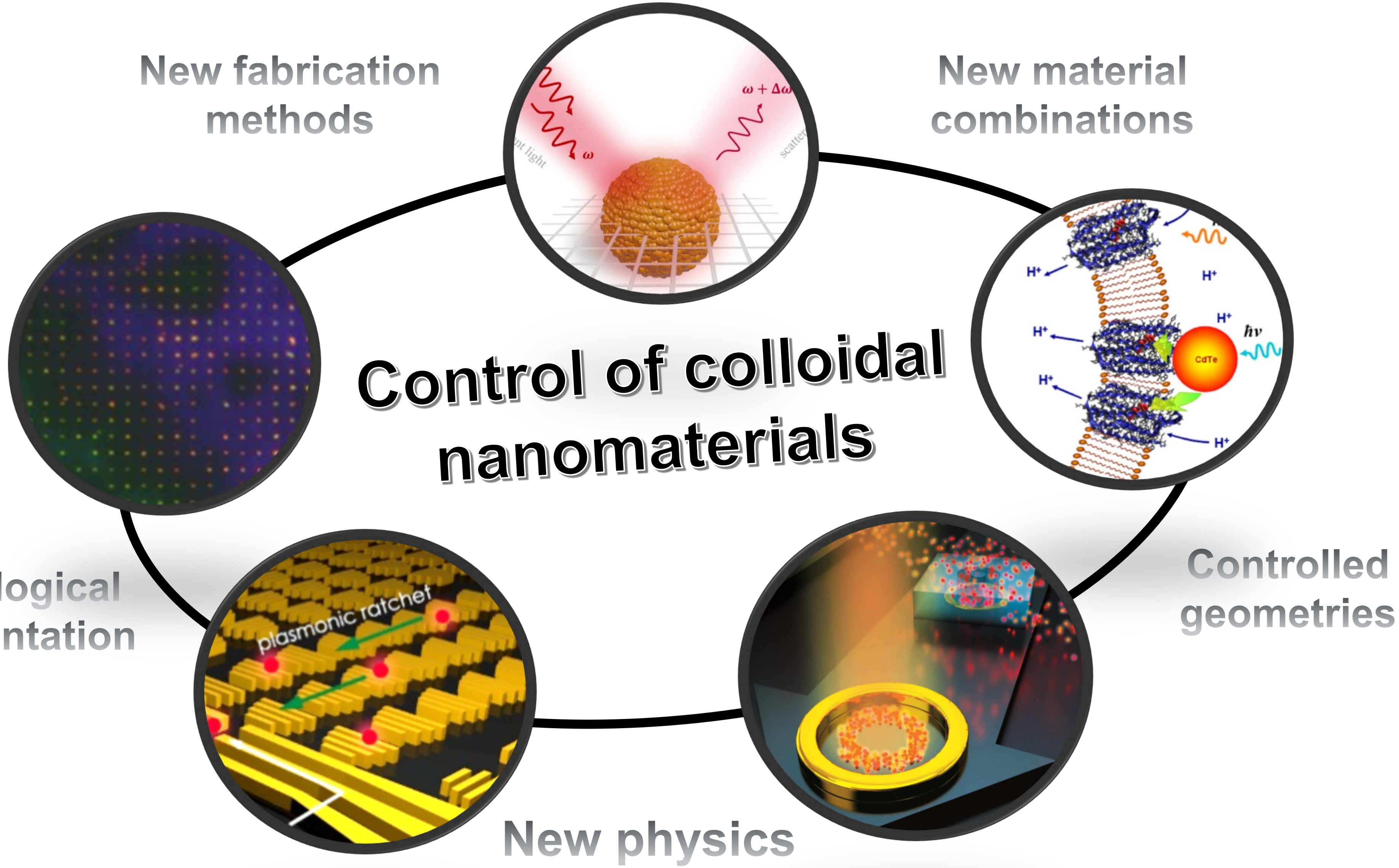
Average speed ~ 2.5 μm/s

Incident power ~2 kW/cm² = 0.2 W/m²

Analytes = ⌀40-200 nm polymer spheres

In preparation

Conclusions



Acknowledgements

People: Select main contributors

Marciano Palma do Carmo (KCL, UK)
Dr. Paloma Huidobro-Arroyo (UAM, Spain)
Dr. Alberto Lauri (ICL, UK*)
Dr. Michael Nielsen (UNSW Sydney, Australia)
Dr. Emiliano Cortes (LMU, Germany)
Prof. Igor Nabiev (URCA, France)
Dr. Pablo Albella (University of Cantabria, Spain)
Dr Francisco Rodríguez Fortuño (KCL, UK)
Prof. Alexander Govorov (Ohio University, USA)
Dr. Mikhail Artemyev (BSU, Belarus)
Dr. Nikolai Gaponik (TUD, Germany)
Prof. Stefan Maier (Monash University, Australia)

Funding:

embarkinitiative – Investing in People and Ideas
reactive plasmonics
The Leverhulme Trust
WITec focus innovations
The Royal Society
EPSRC Engineering and Physical Sciences Research Council
European Science Foundation

References:

QD as artificial LH antenna for RCs
Angew. Chem. Int. Ed. **49**, 7217 (2010)

QD as artificial LH antenna for bR protein
NanoLett. 10, 2640 (2010)

Superclusters of metallic nanoparticles
ACS Photonics 4, 2070-2077 (2017)

QD as probes for waveguide characterization
NanoLett. 16, 1410-1414 (2016)

QDs-Plasmonic Ring Cavities coupling
ACS Nano 9, 2648-2658 (2015)

Template dissolution method
ACS Nano 14, 17693 (2020)

Contact:

aliaksandra.rakovic@kcl.ac.uk
http://nanobiophotonics-group.com/

Thank you for your attention!