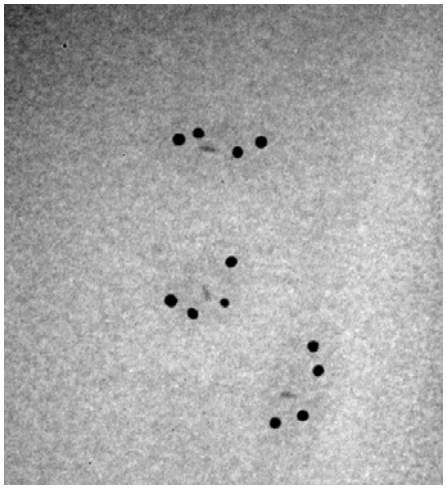
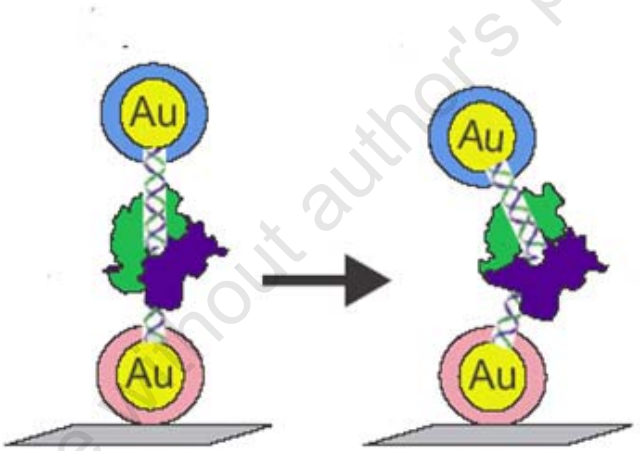
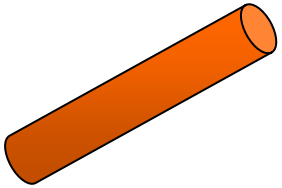
Nanocrystal Molecules and plasmon ruler study of ECO RV DNA cleavage

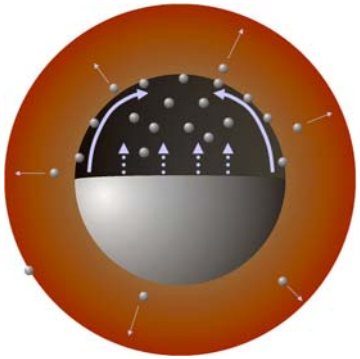
Björn Reinhardt, Sassan Sheikolislami,
(Carsten Sönneschsen), Prof. Jan Liphardt

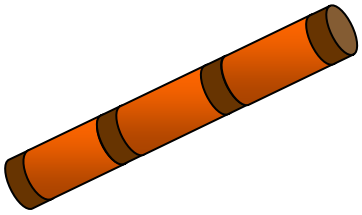




New nanocrystals for biological imaging applications

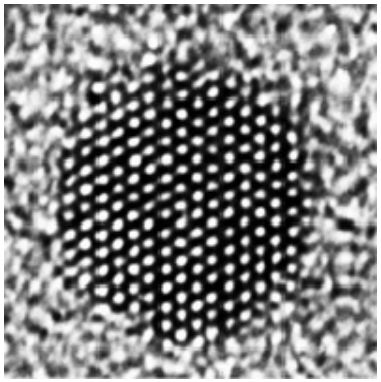


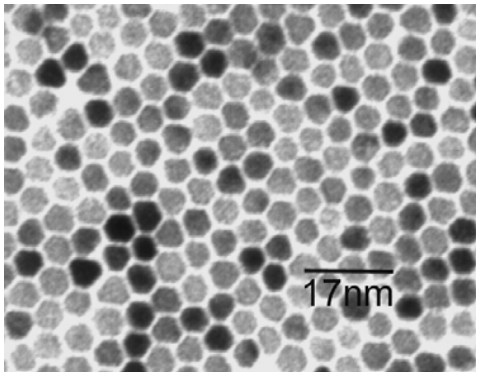


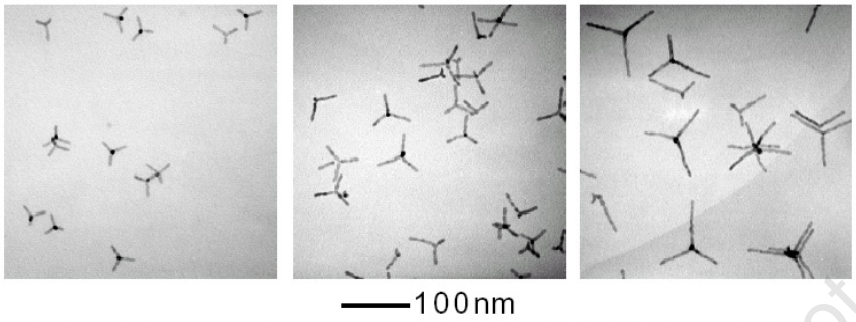


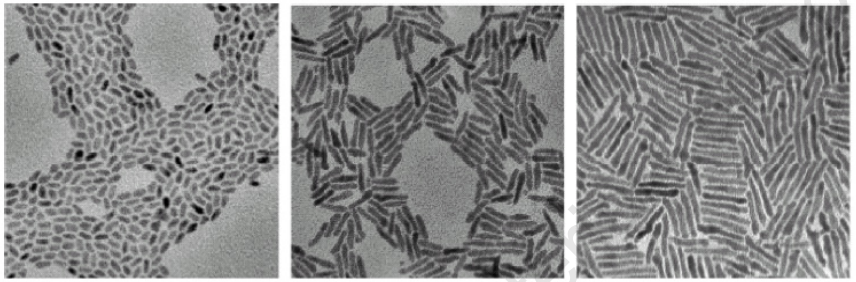
Paul Alivisatos
Lawrence Berkeley National Lab and University of California, Berkeley

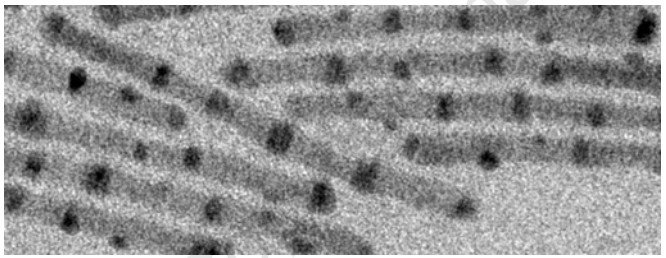
Colloidal inorganic nanocrystals as building blocks for new materials

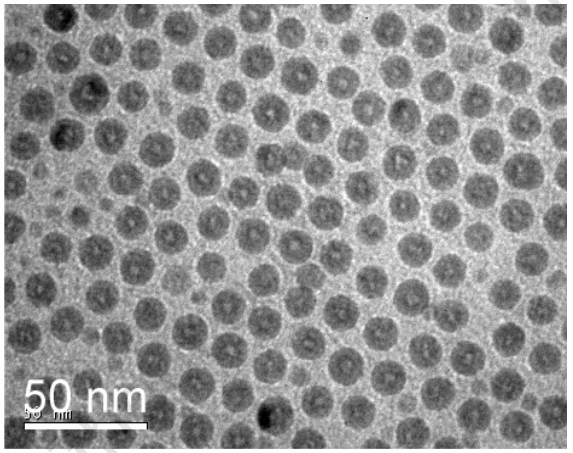


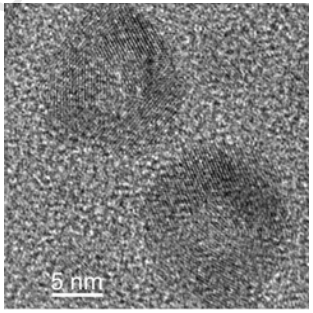


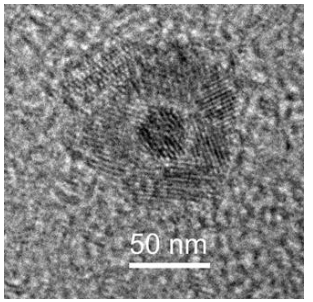


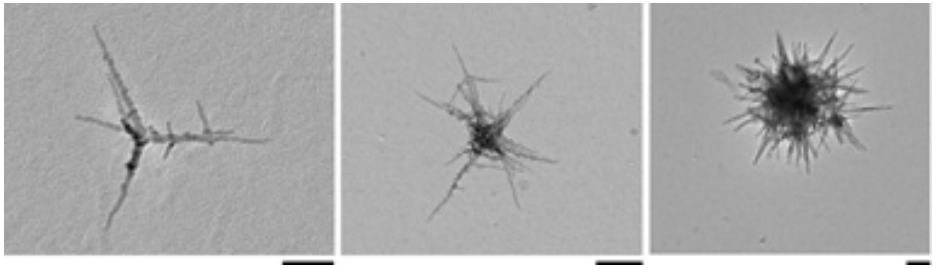


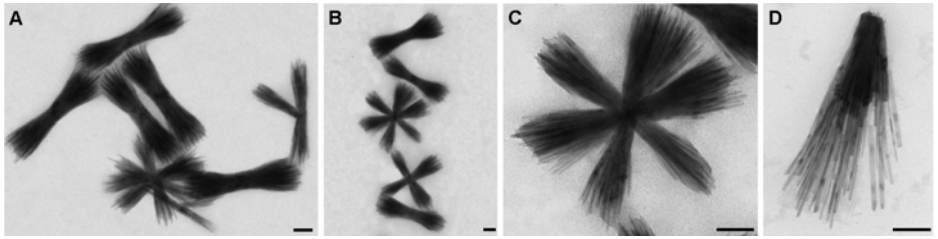






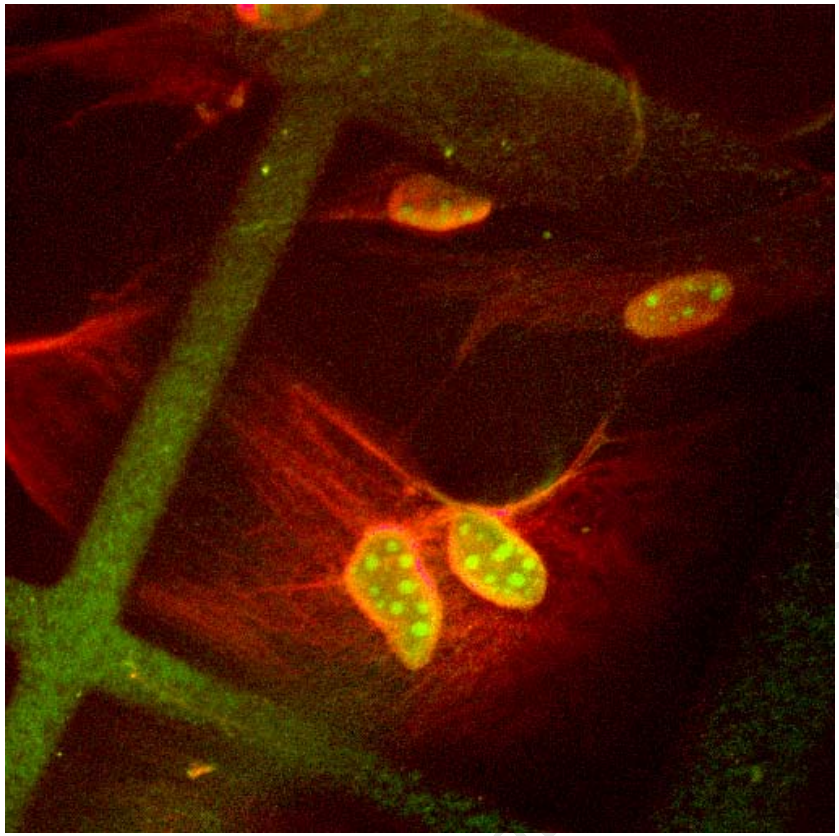






Symmetry, topology, connectivity…

Quantum Dot Cell Labeling

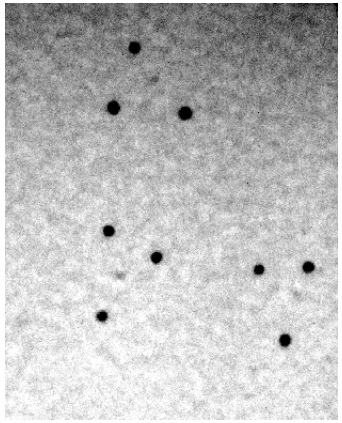


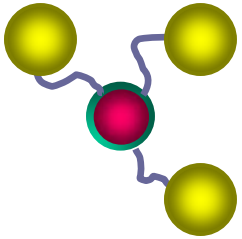
Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P., *Science* **1998**, *281*, 2013-2016.

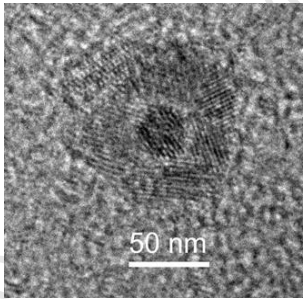
Chan, W. C. W.; Nie, S. M., Science **1998**, *281*, 2016-2018.

From artificial atoms to artificial molecules: coupled inorganic nanocrystals

Plasmonic Coupling

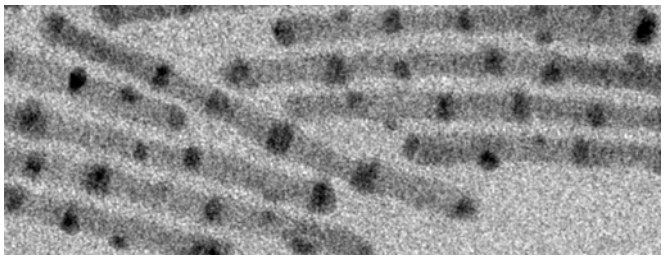


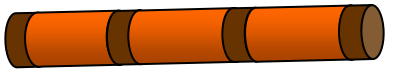




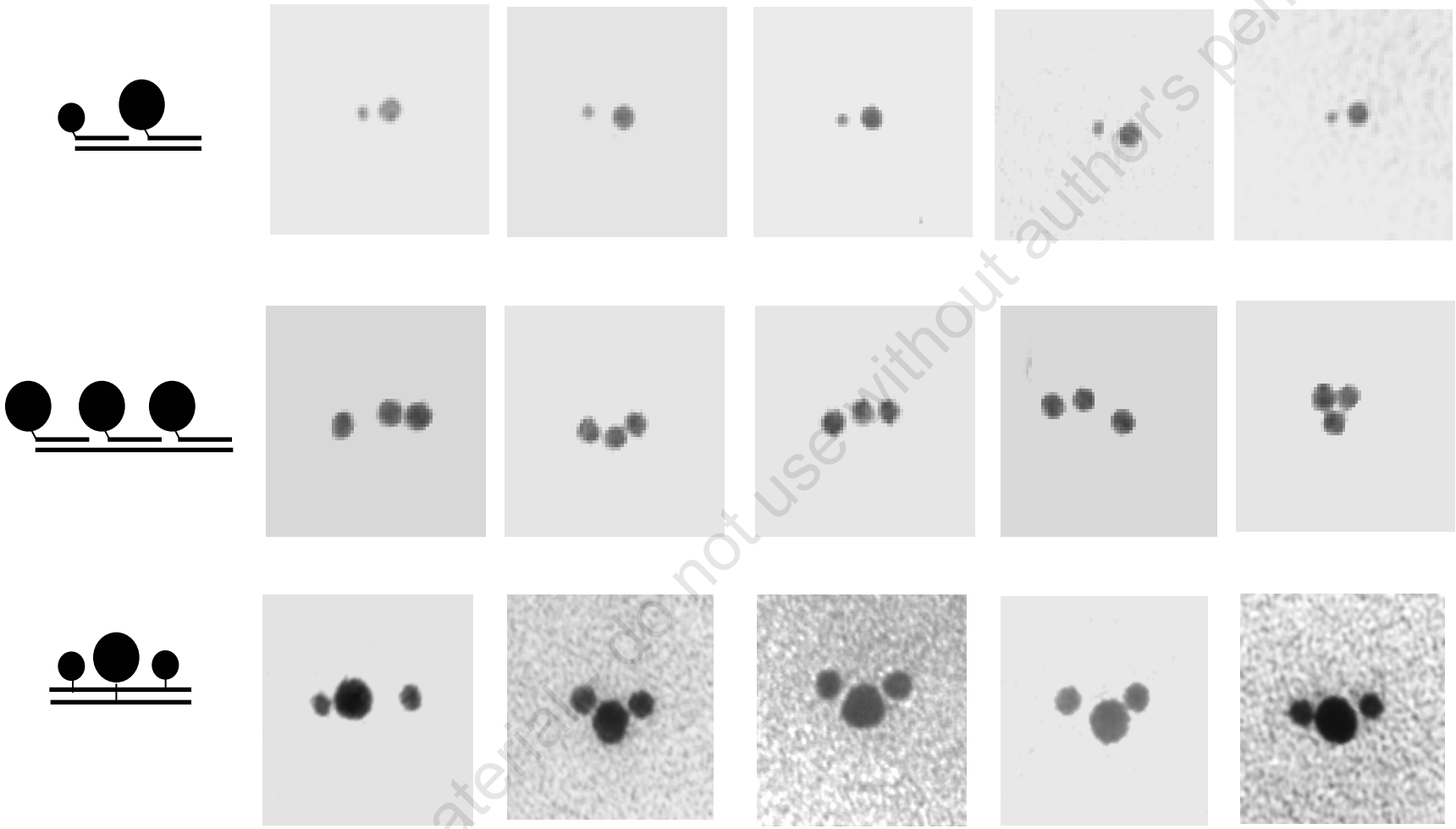
Chemical Coupling

Electronic Coupling





DNA-directed grouping of nanocrystals

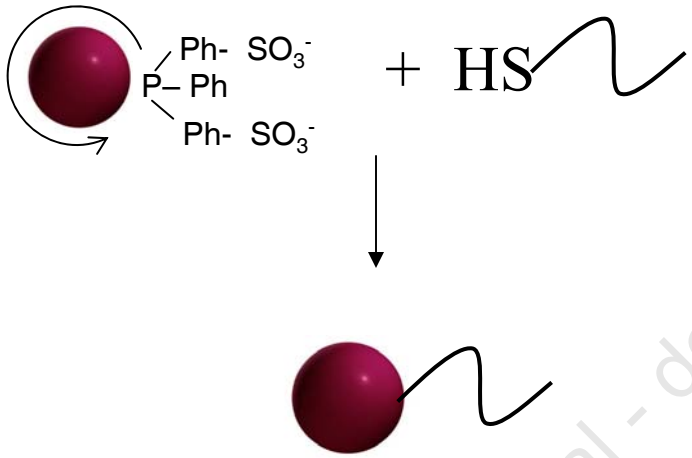


Alivisatos and Schultz , Nature 382 p. 609 1996; Angew. Chemie 38 p. 1808 1999
related work by (Mirkin and Letsinger,)

DNA conjugation and electrophoresis of Au nanocrystals

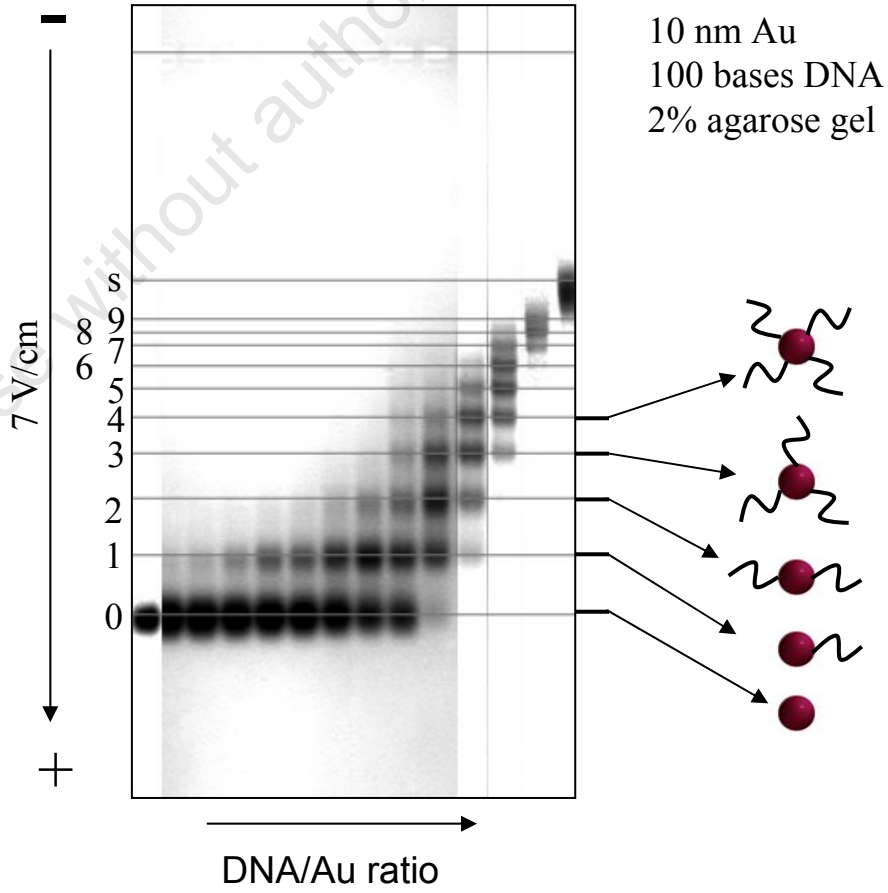
DNA can be directly attached to Au surface via thiol-linkage

Tri-phenyl phosphine sulfonate coated Au



Au and DNA are negatively charged

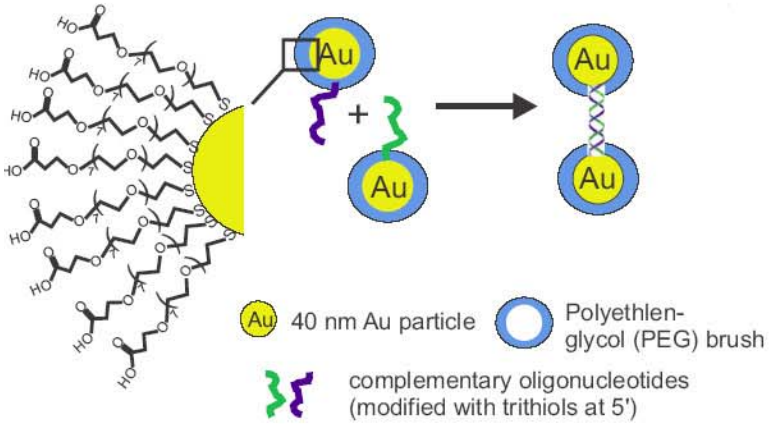
Gel electrophoresis of Au nanocrystal / DNA conjugates

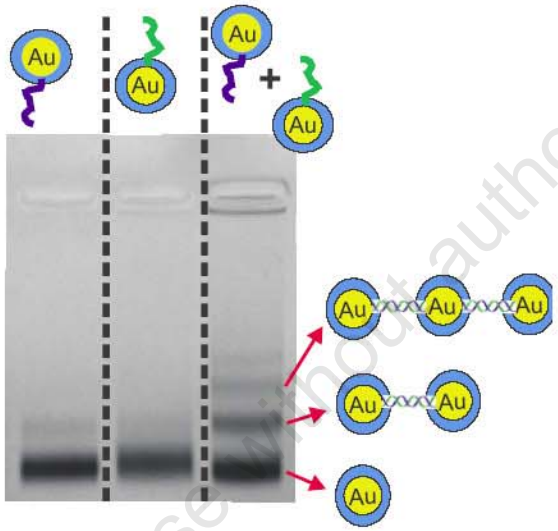


Zanchet et al. *Nano Letters*, **2001**, *1*, 32.

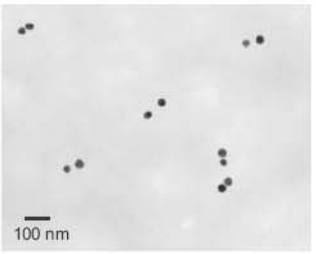
-> Au nanocrystals with controlled number of DNA molecules

Isolation of discrete particle groupings by electrophoresis

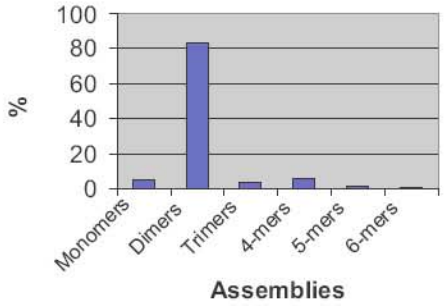




TEM of gel-isolated
60 bps dimers



TEM confirms "Dimer Band" highly
enriched in DNA-linked dimers

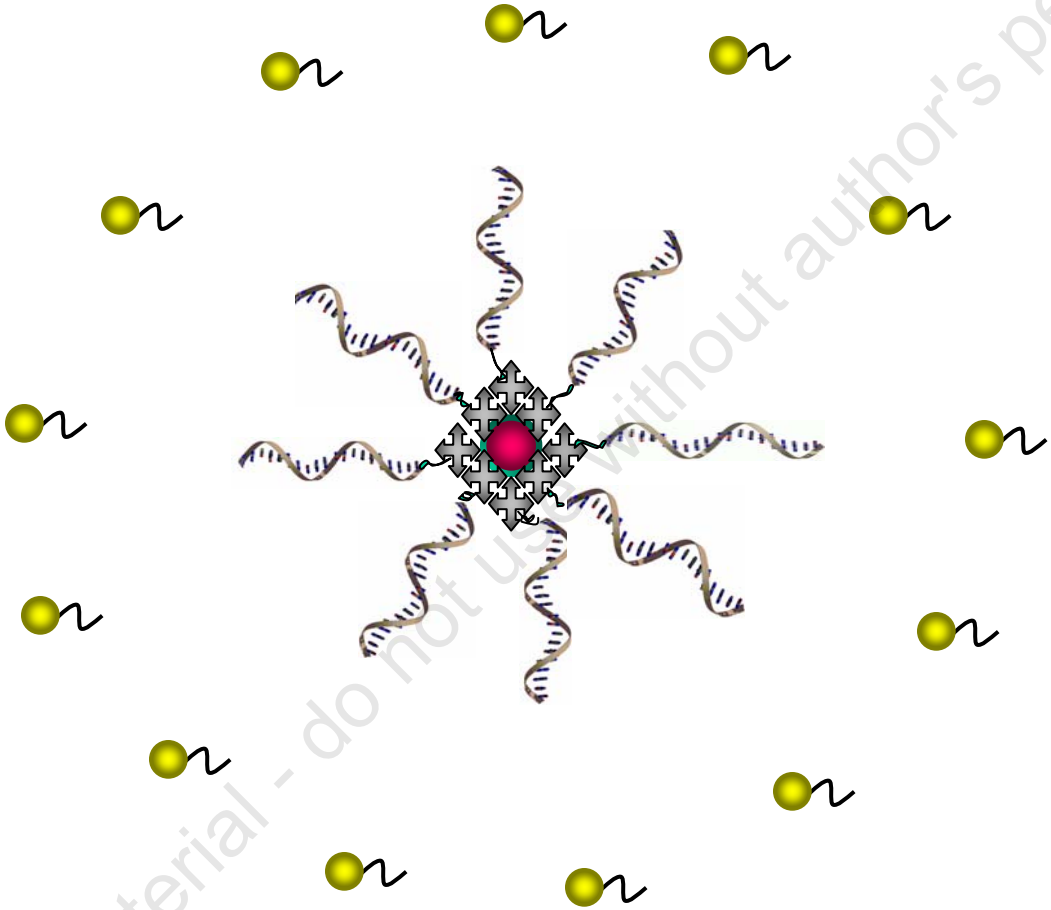


Alivisatos, Johnsson, Peng, Wilson, Loweth, Bruchez, Schultz, *Nature* **1996,** 382, (6592), 609-611.

Zanchet, Parak, Gerion, Alivisatos, *Nano Letters* **2001,** 1, (1), 32-35.

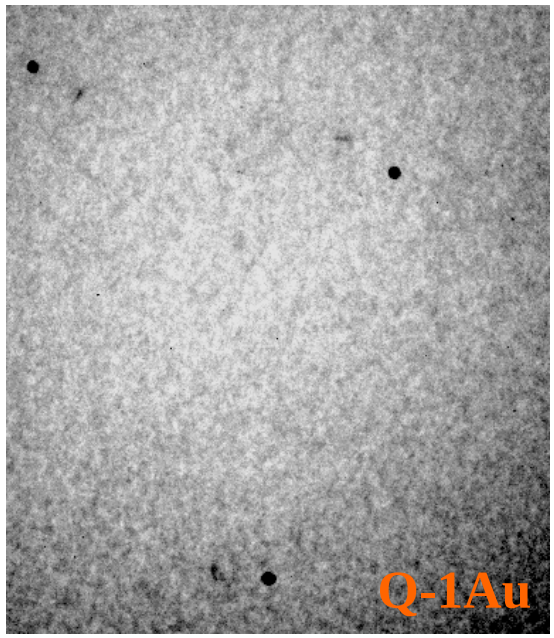
Fu, Micheel, Cha, Chang, Yang, Alivisatos, *JACS* **2004,** 126, (35), 10832-10833.

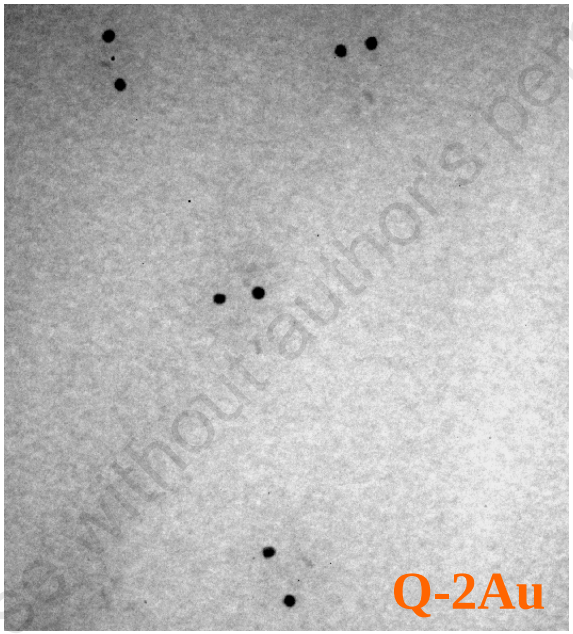
DNA Directed Assembly of DISCRETE Colloidal Quantum Dot – Au nanocrystal groupings

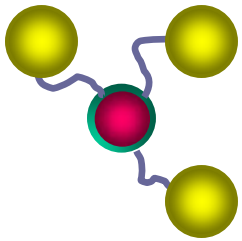


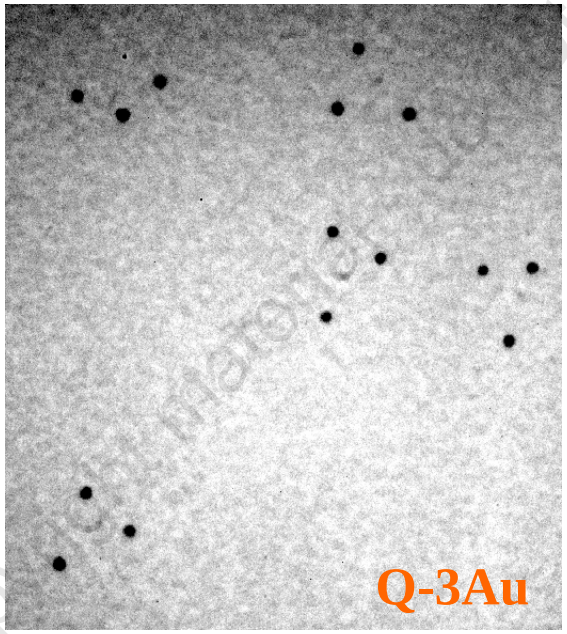
Discrete Nanostructures of Quantum Dots/Au with DNA
Fu, A.; Micheel, C. M.; Cha, J.; Chang, H.; Yang, H.; Alivisatos, A. P.;
J. Am. Chem. Soc.; (Communication); **126**(35): 10832-10833 (2004).

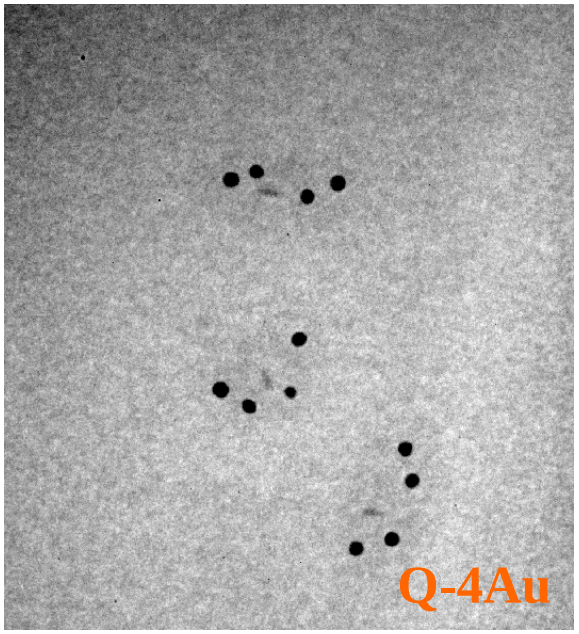
TEM Images of QDot-Au conjugates





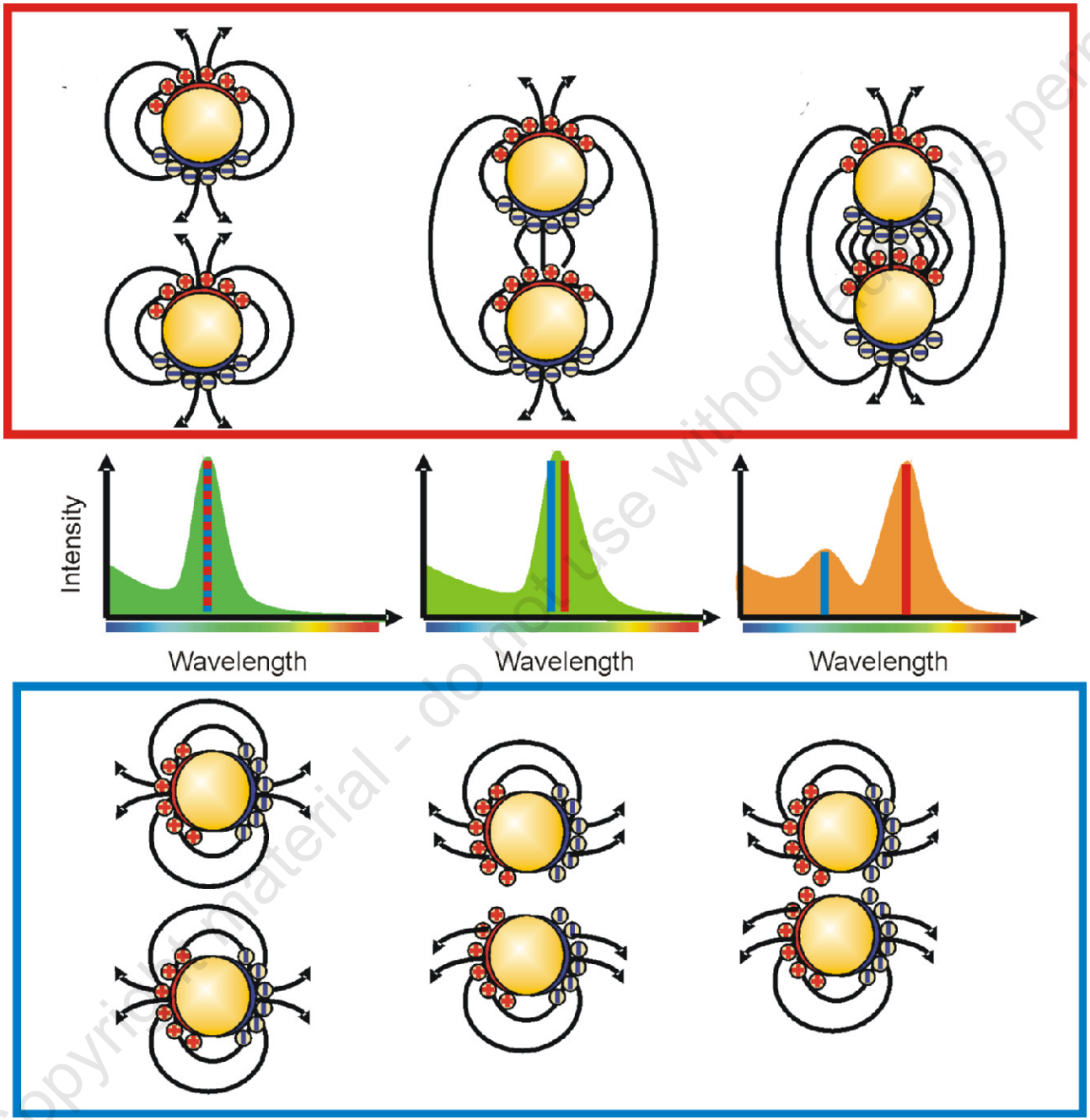




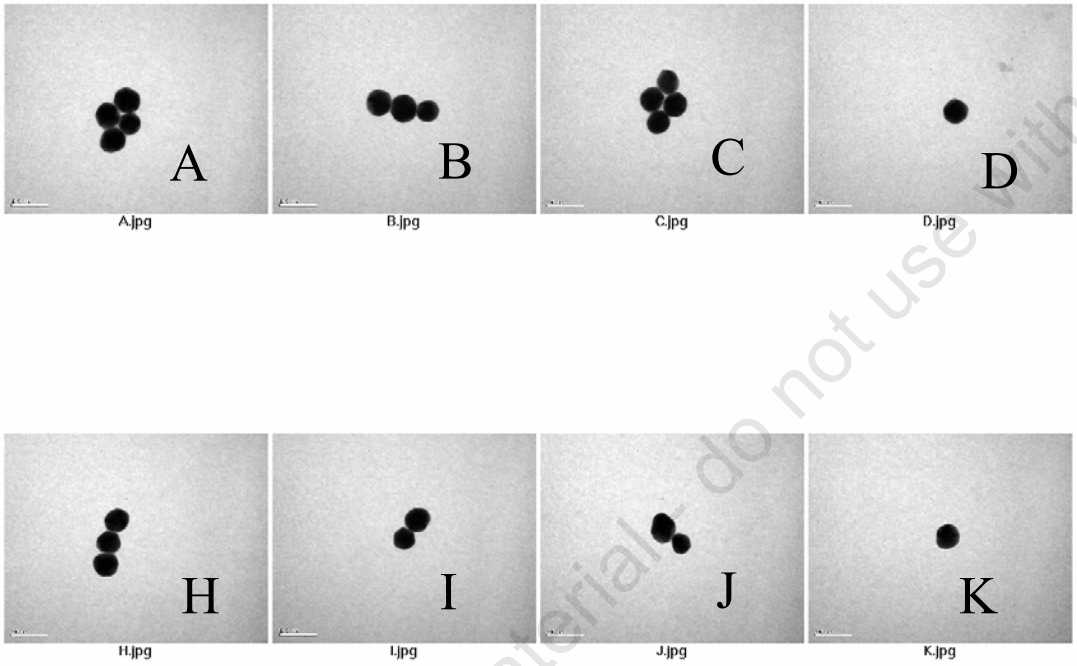


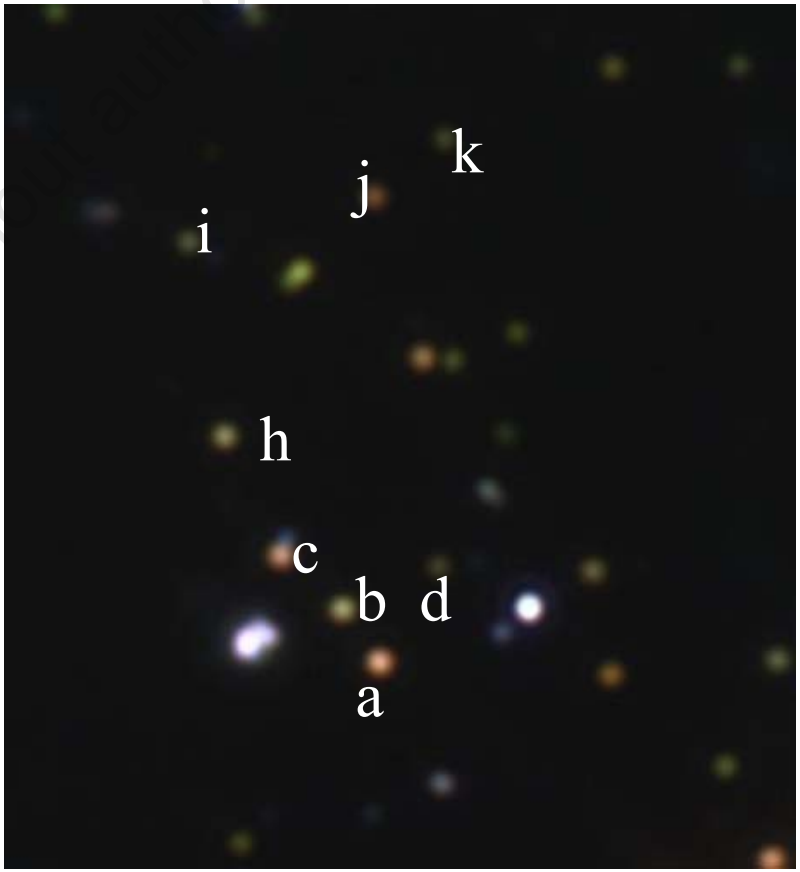
Au Size: 10nm

Plasmon coupling



Correlating optical and TEM images

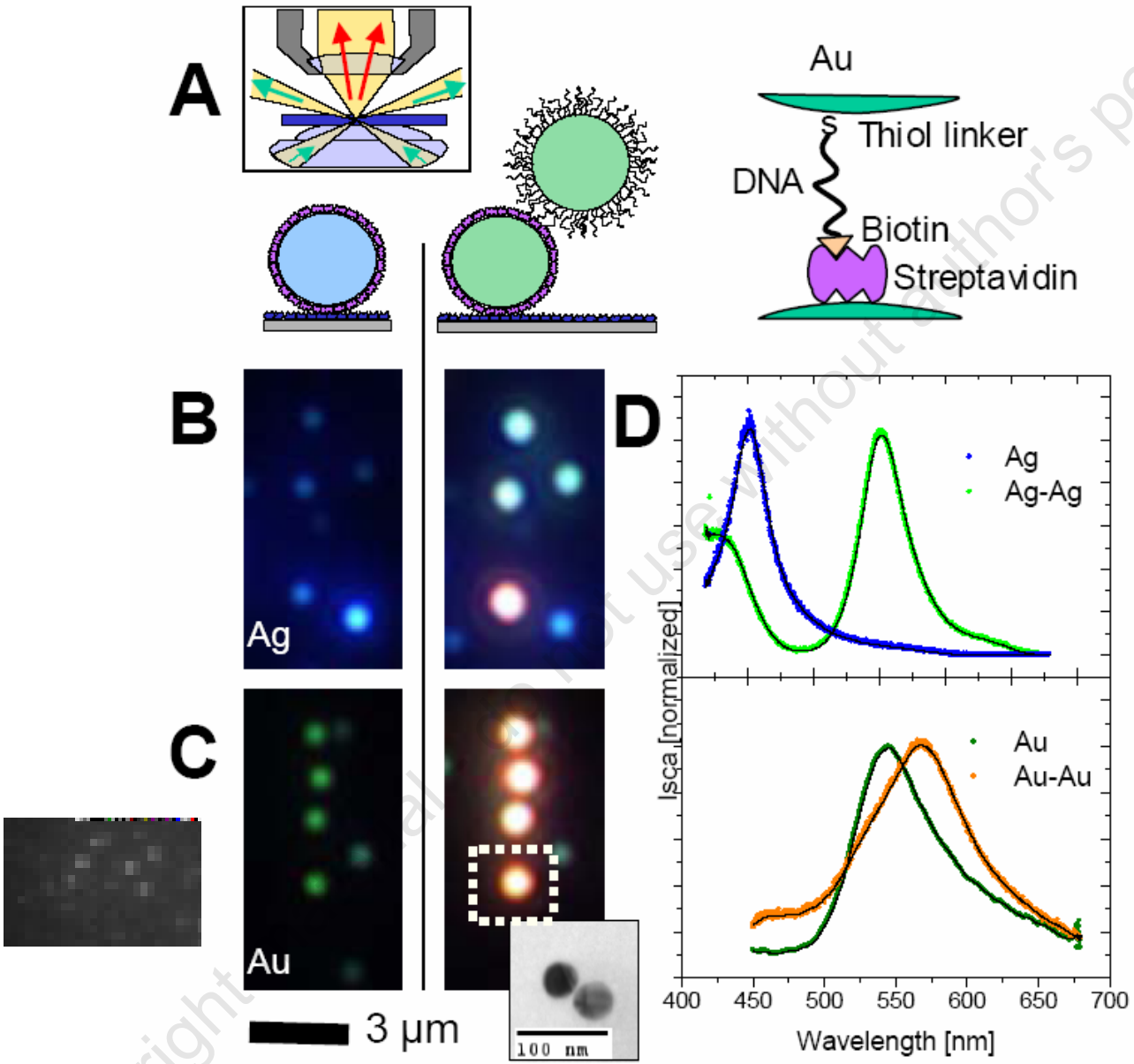




50nm Au

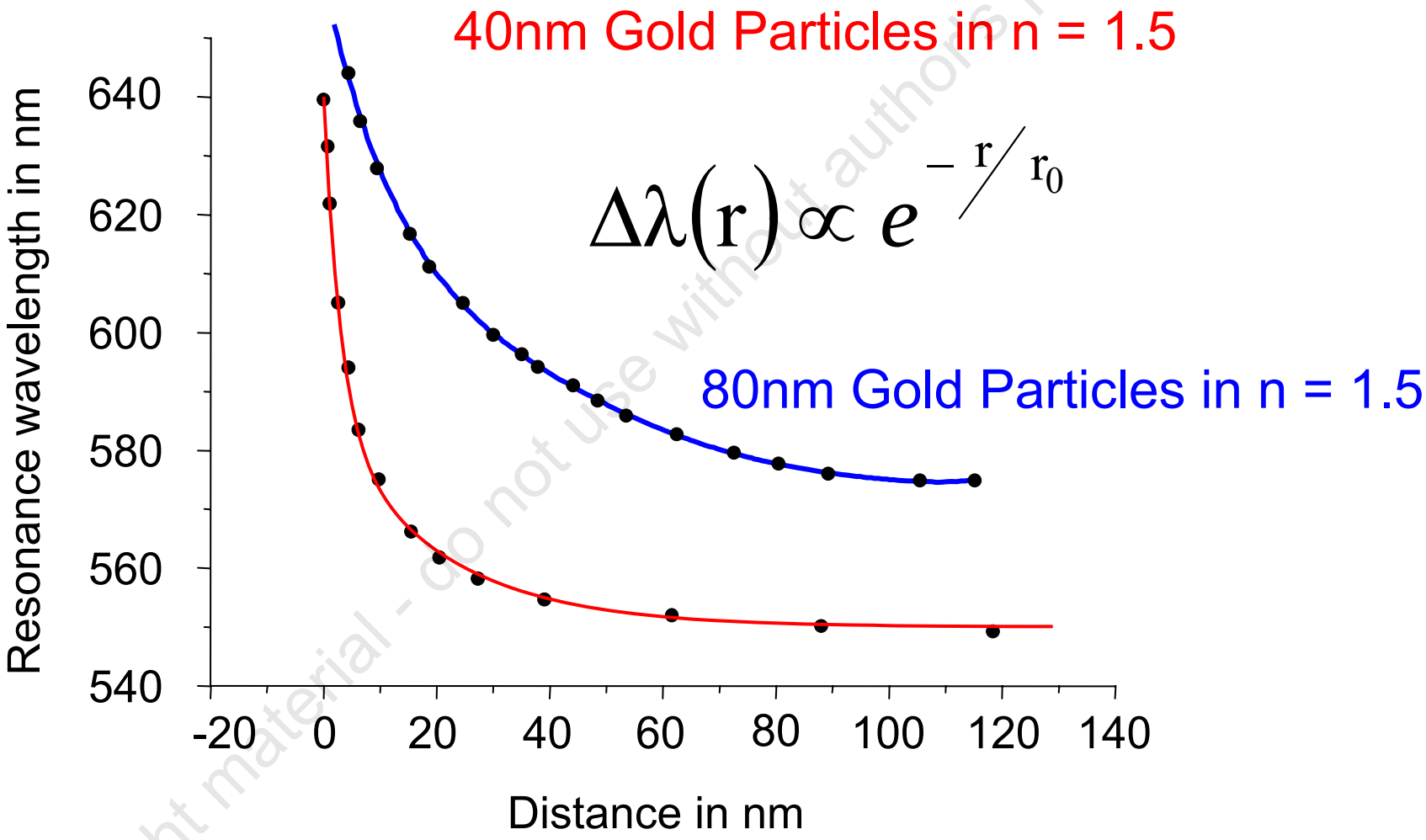
Carsten Sönneschen

Light Scattering from Ag or Au Particle Pairs



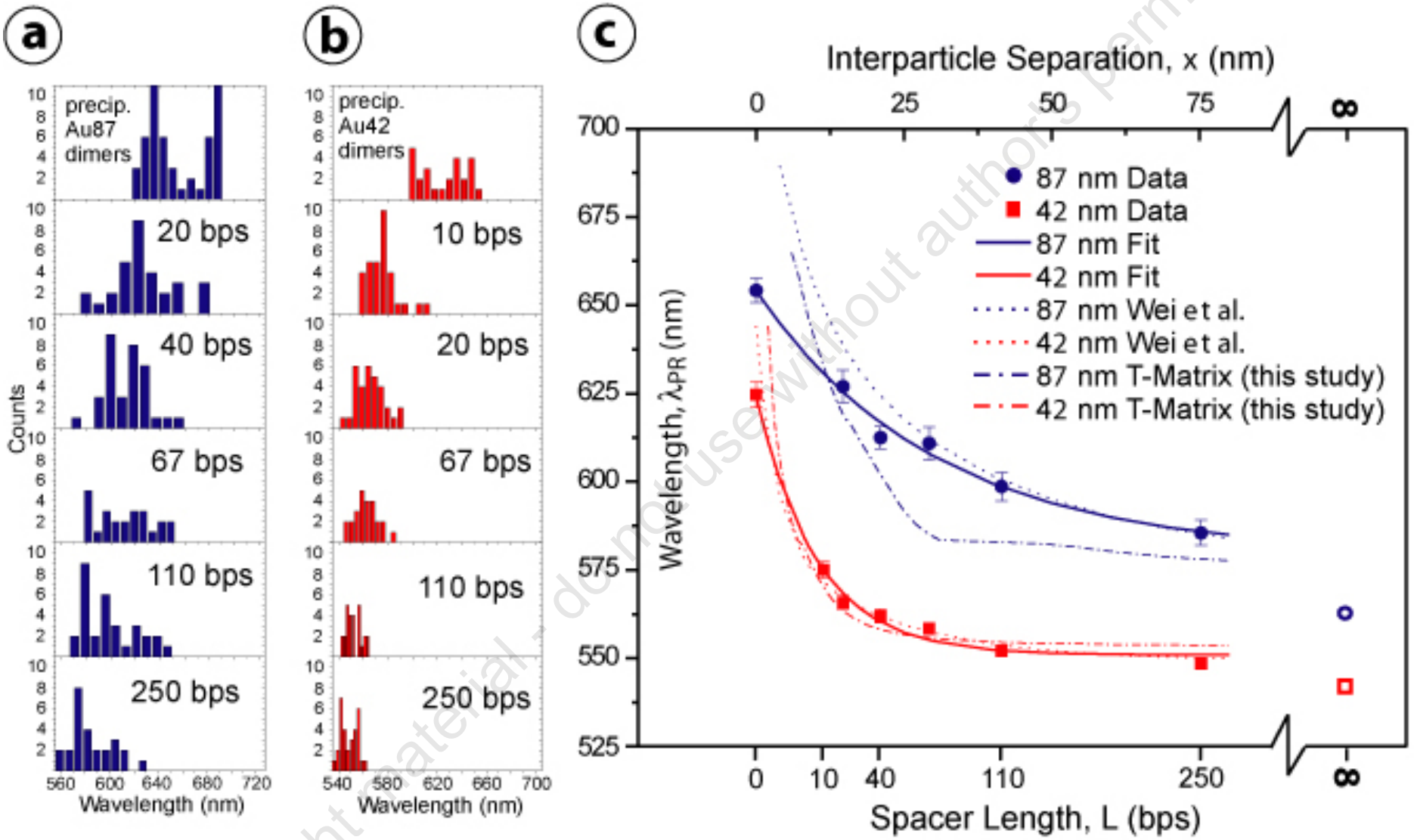
Sonnichsen, C., B. M. Reinhard, J. Liphardt and A. P. Alivisatos Nature Biotechnology 23(6): 741-745(2005). "A molecular ruler based on plasmon coupling of single gold and silver nanoparticles.".

Possibility of Au nanoparticle dimers as macromolecular ruler?



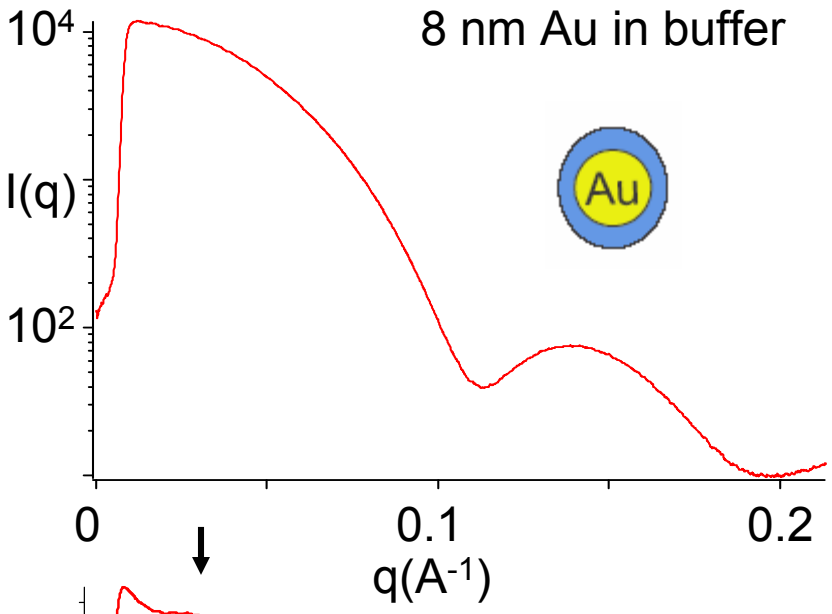
From Wei, Su, Durant, and Zhang, Nano Letters,1076 (2004) T-Matrix simulation

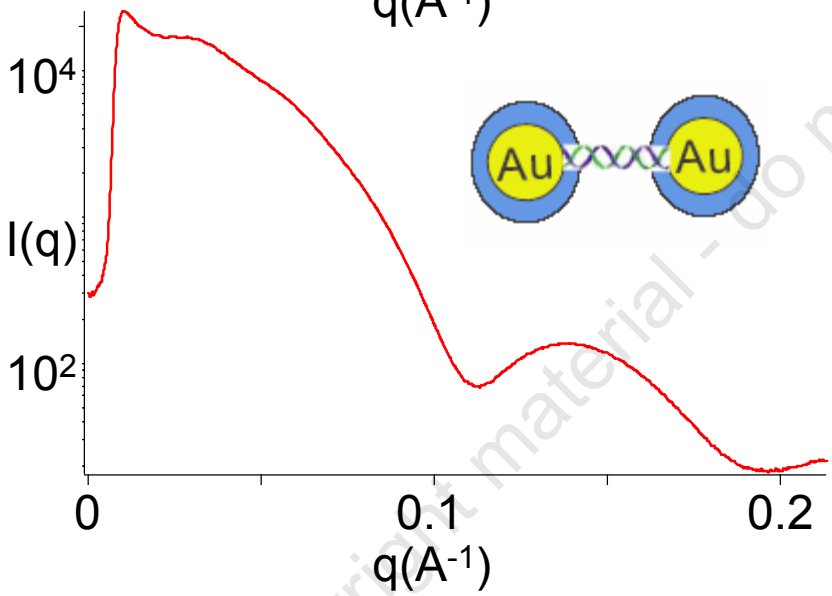
Calibration of the Plasmon Spectroscopic Ruler

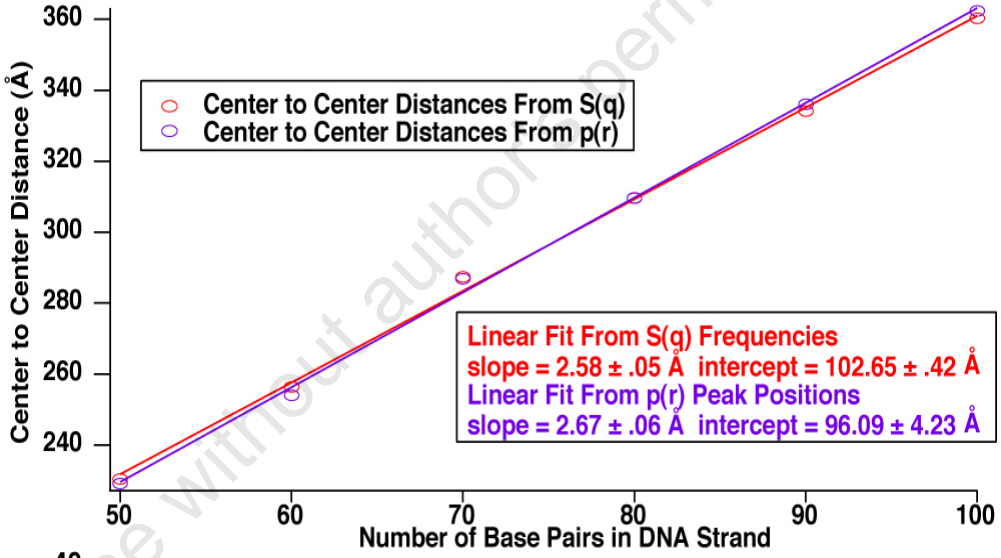


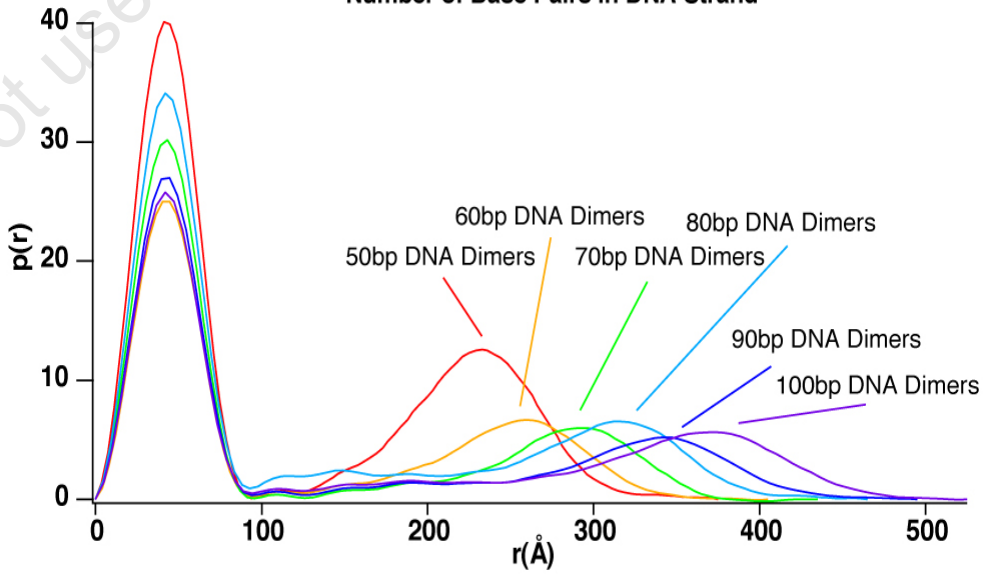
Calibration of Dynamic Molecular Rulers Based on Plasmon Coupling between Gold Nanoparticles
Reinhard, B. M.; Siu, M.; Agarwal, H.; Alivisatos, A. P.; Liphardt, J. Nano Lett; 2005; 5(11); 2246-2252.

SAXS Studies of DNA-directed Au Dimer Distances



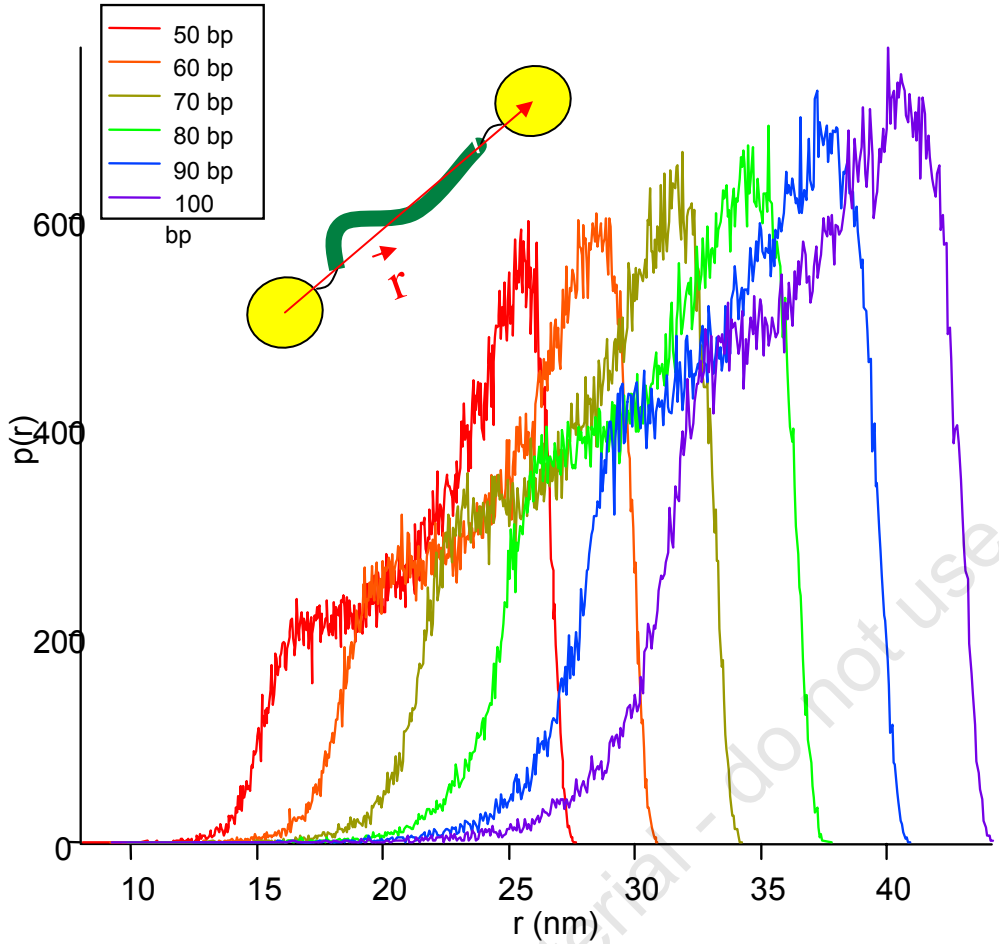


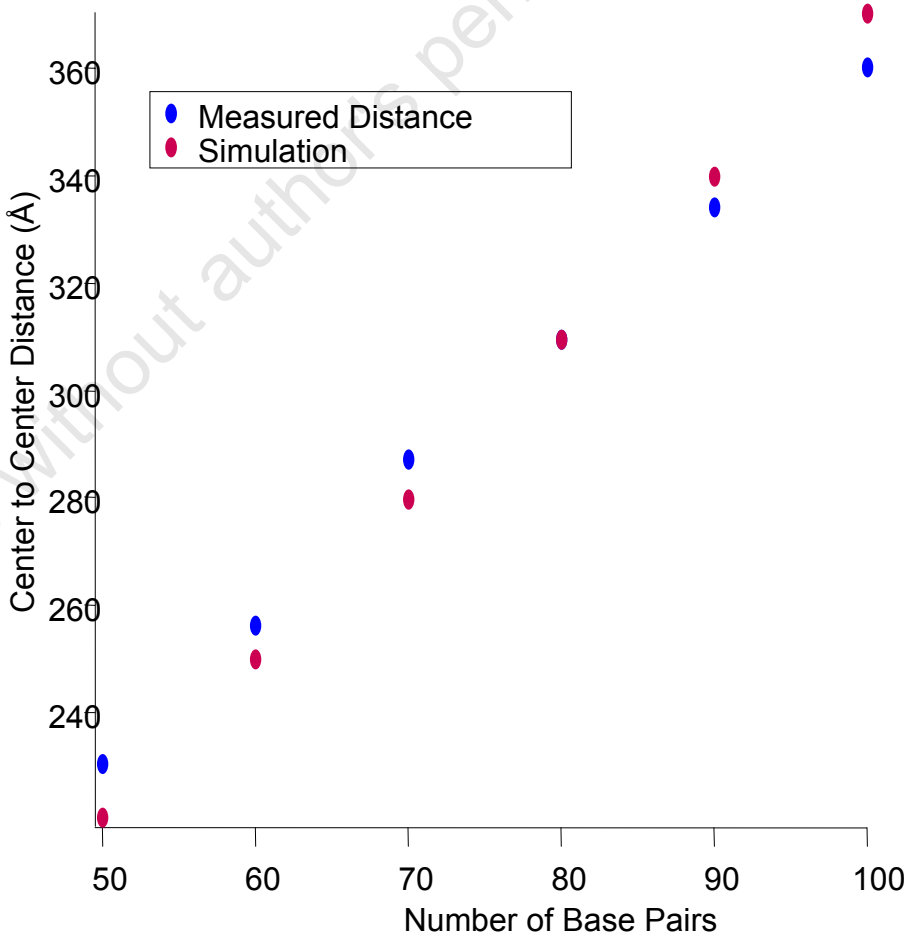




Alex Mastroianni

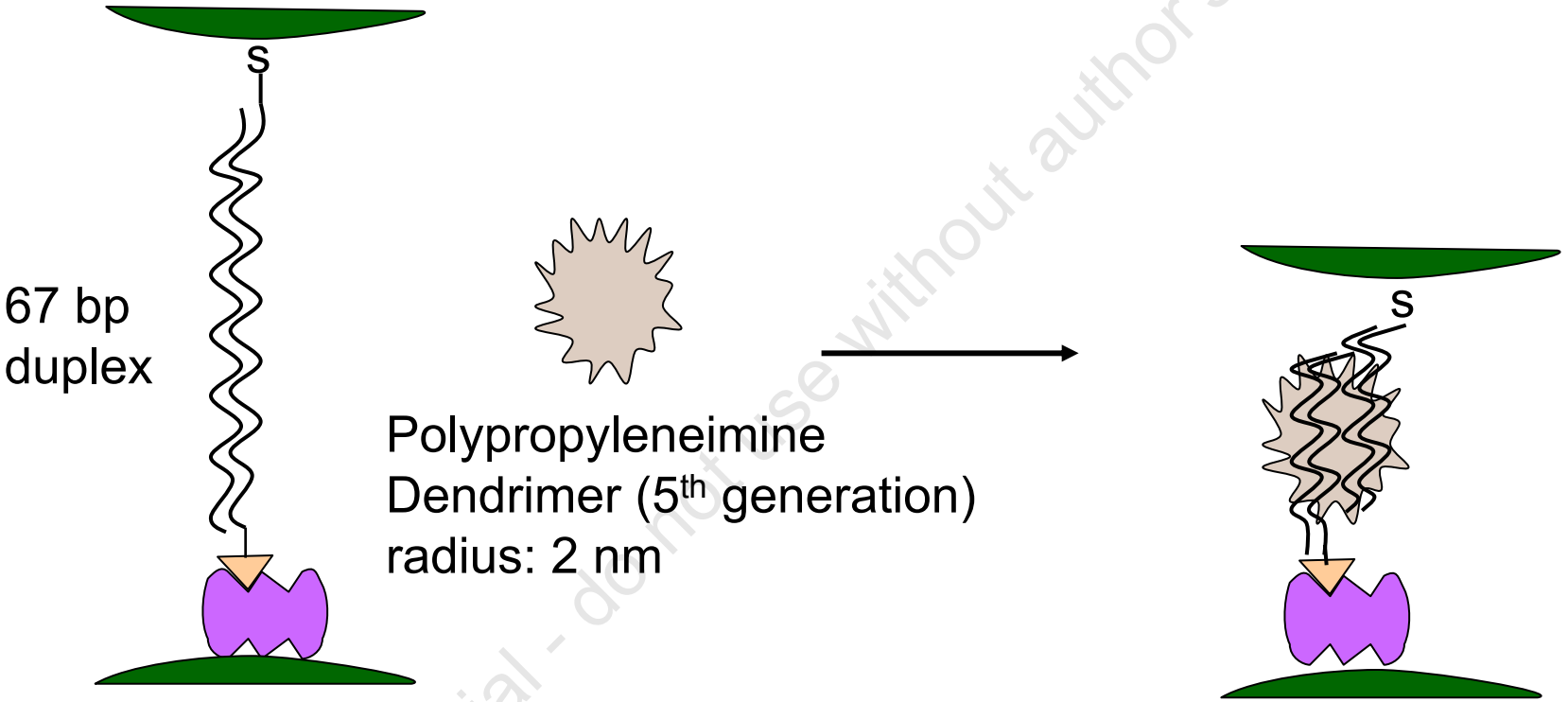
Monte-Carlo Simulations of inter-particle distance distribution





David Sivak and Prof. Phillip Geiisler

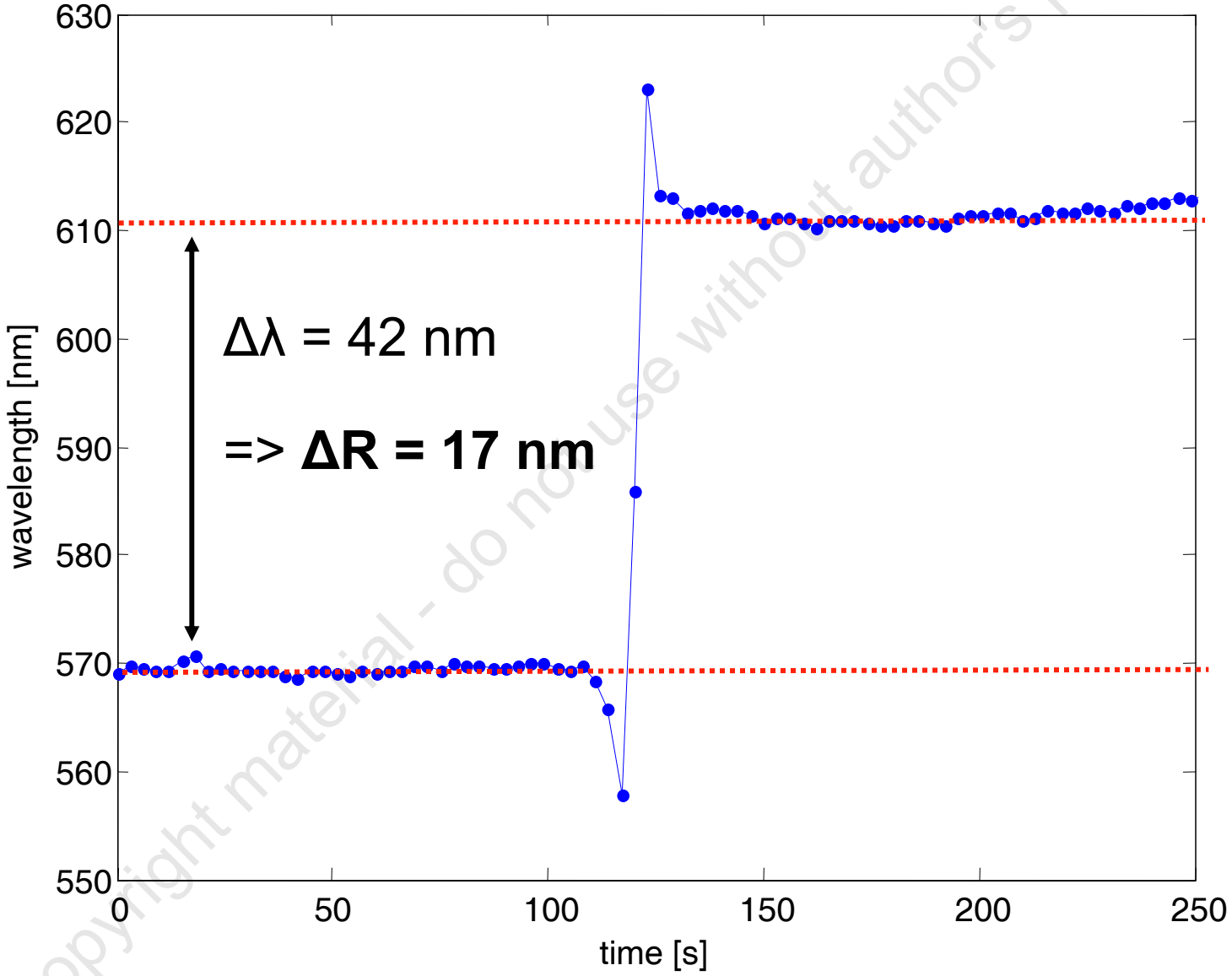
DNA condensation by dendrimers



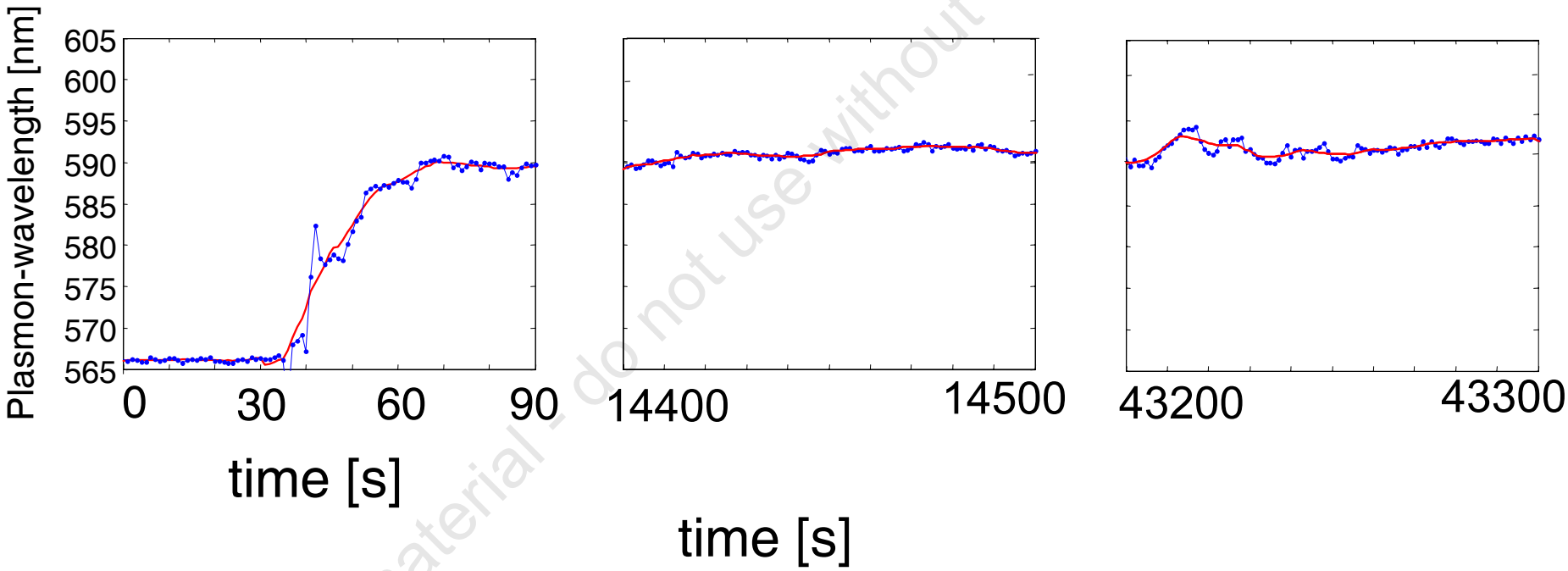
DNA chain wrapped 1.75 times around dendrimer:

ΔR ~ 18.0 nm

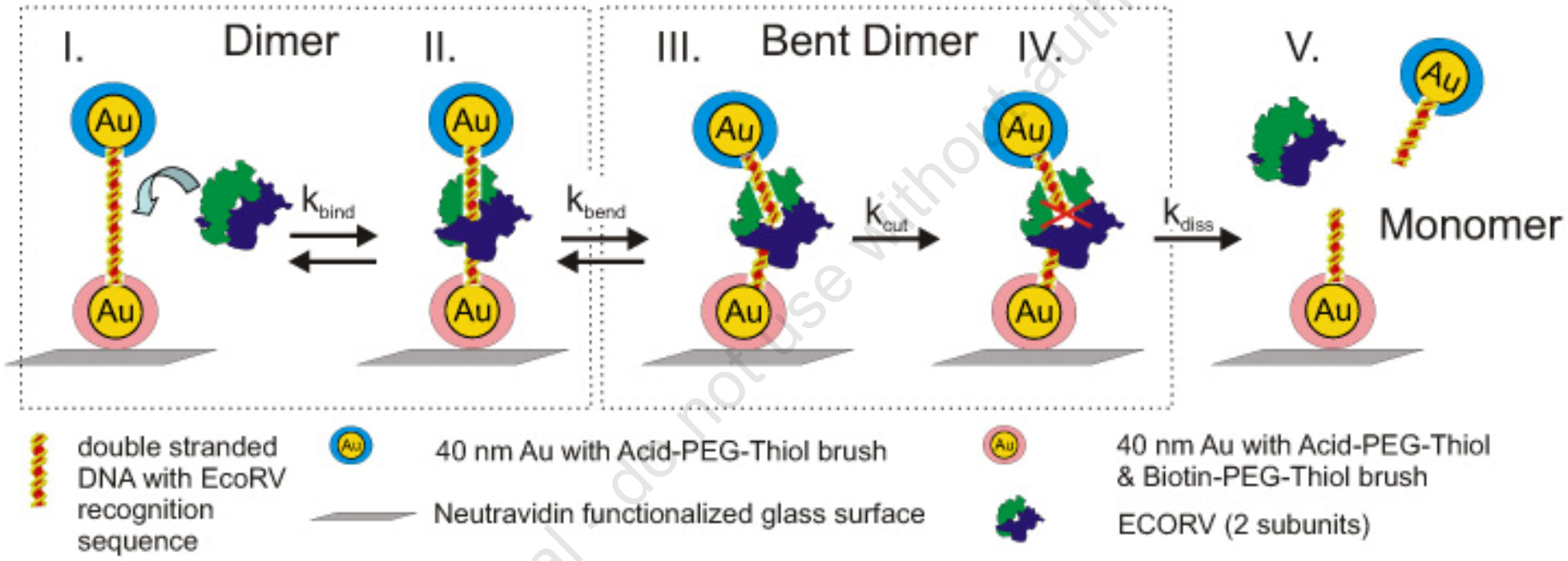
Dendrimers induce large red shift



Spermidine binding to DNA

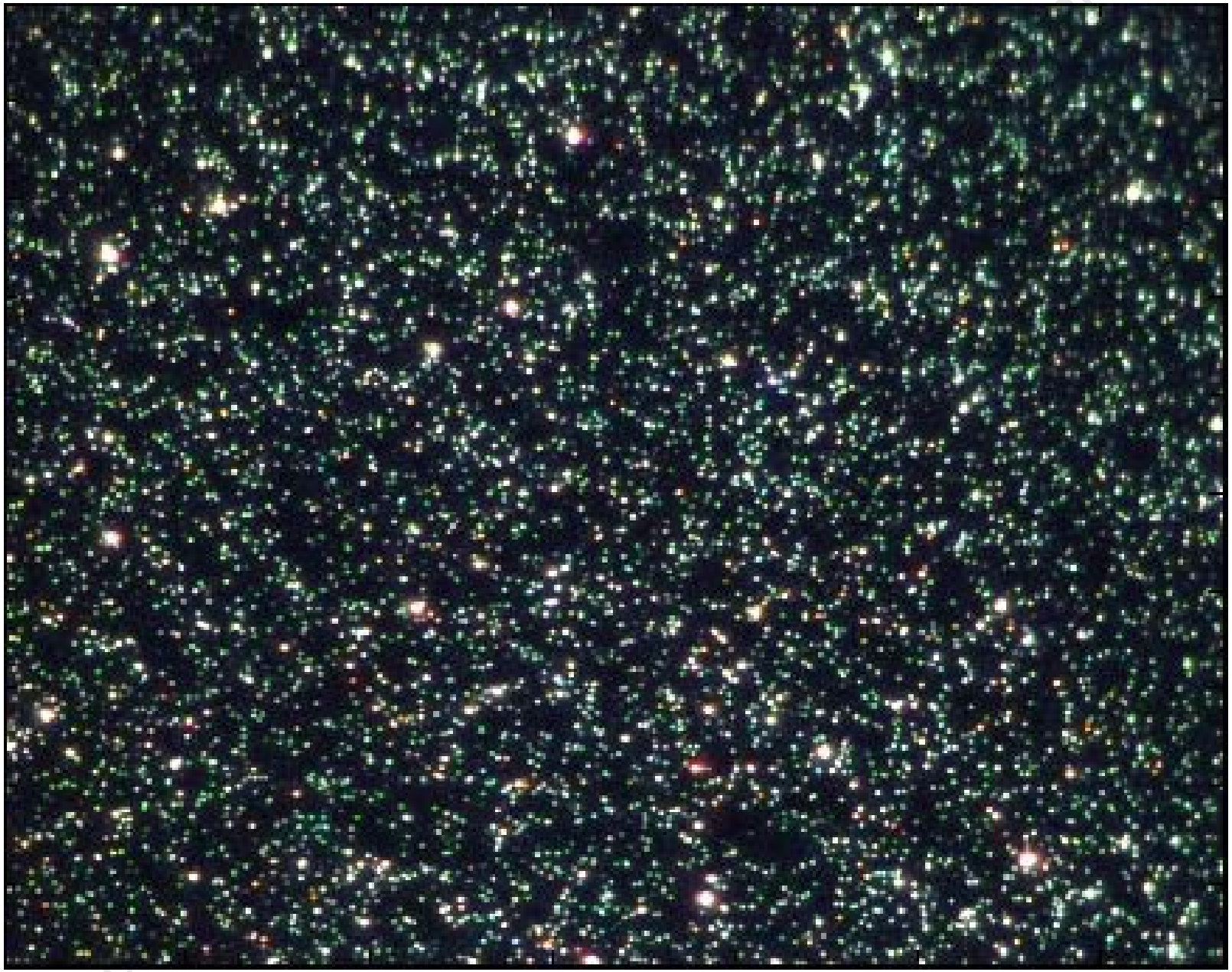


Application of the plasmon ruler to DNA cleavage by the ECORV restriction enzyme

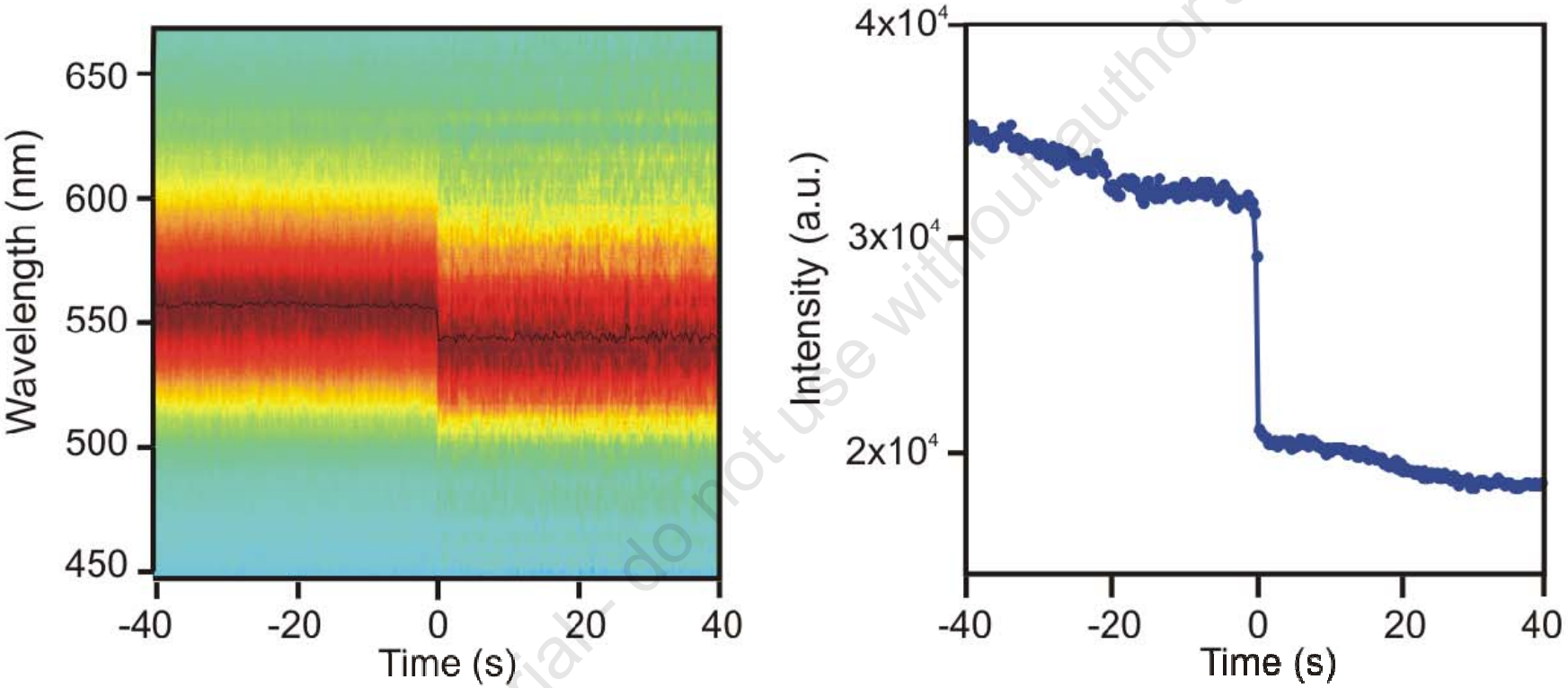


Björn Reinhardt, Sassan Sheikholislami, Prof. J. Liphardt

Single molecule cleavage events readily seen

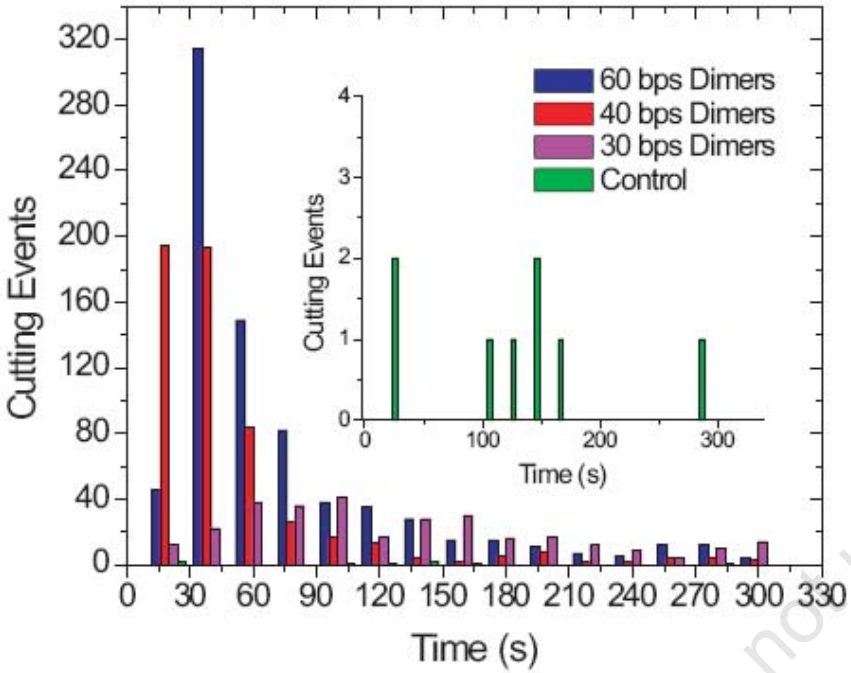


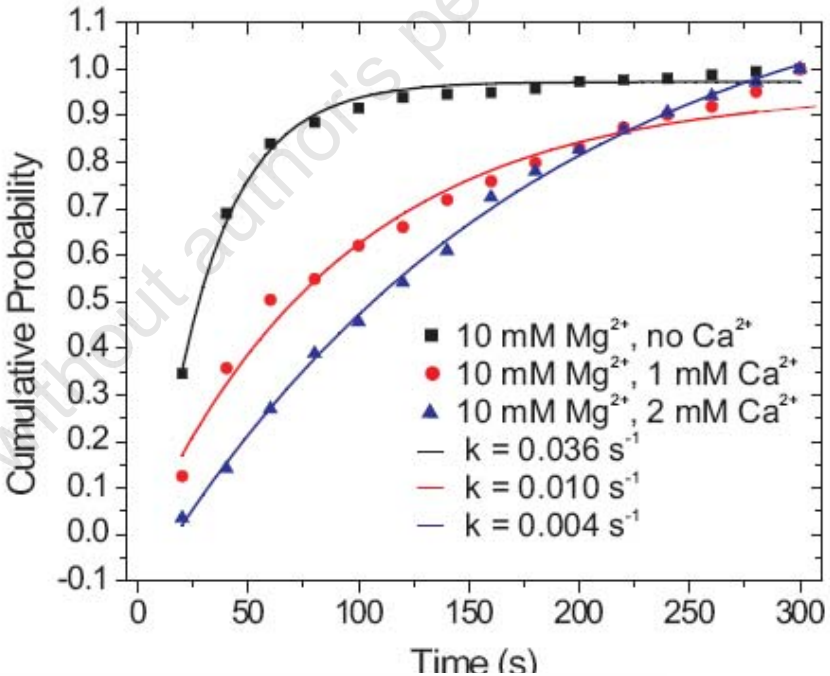
Spectral signature of cleavage correlates with intensity change

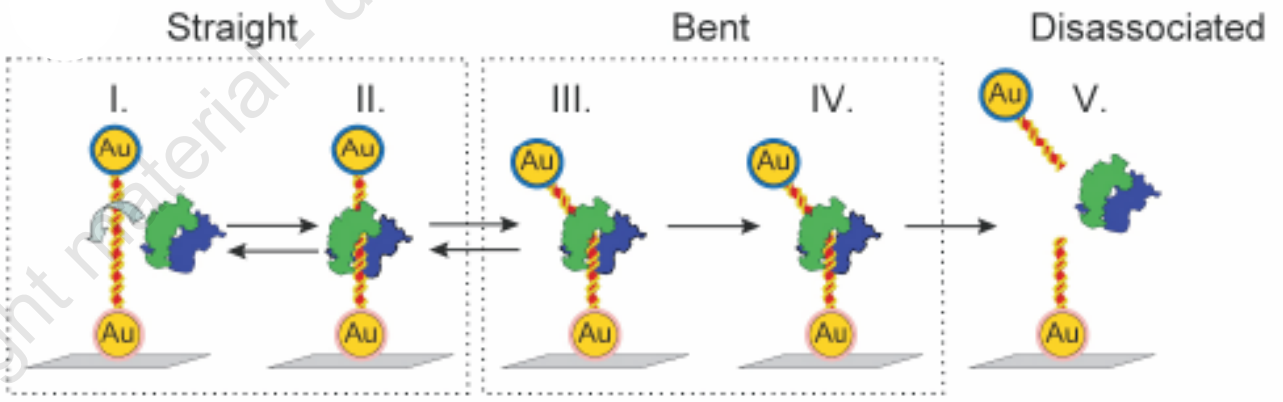


No blinking
No bleaching

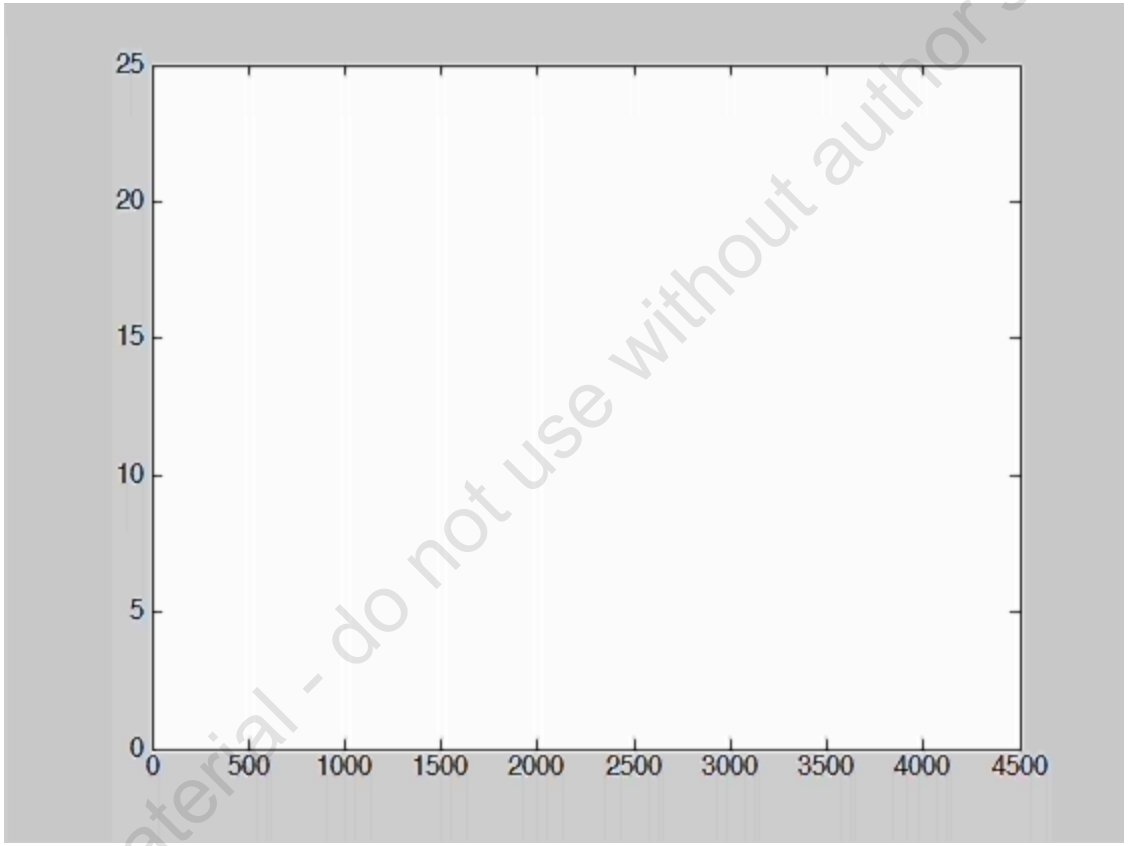
Ensemble kinetic measurements reproduce bulk data







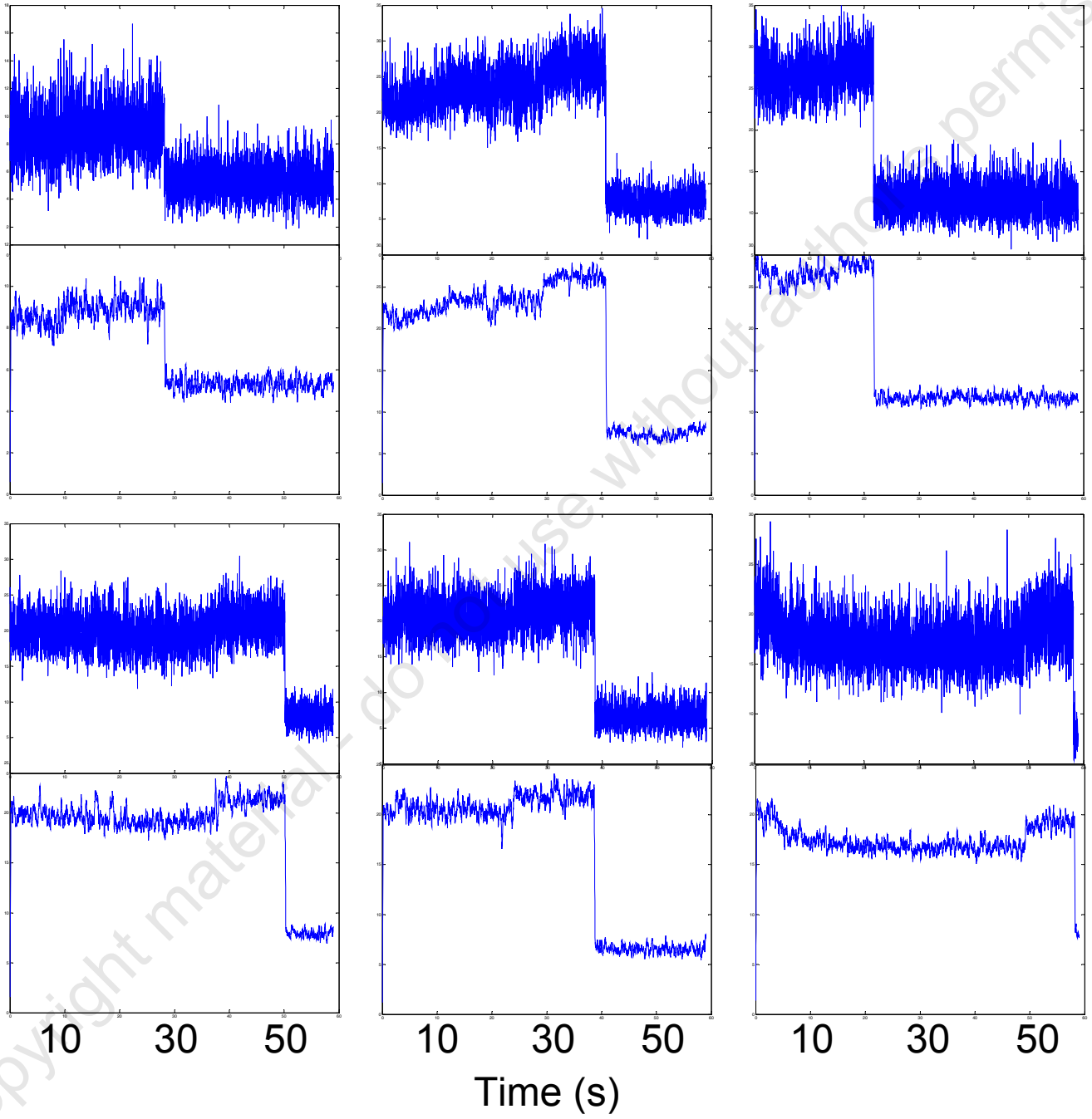
One cutting trajectory…



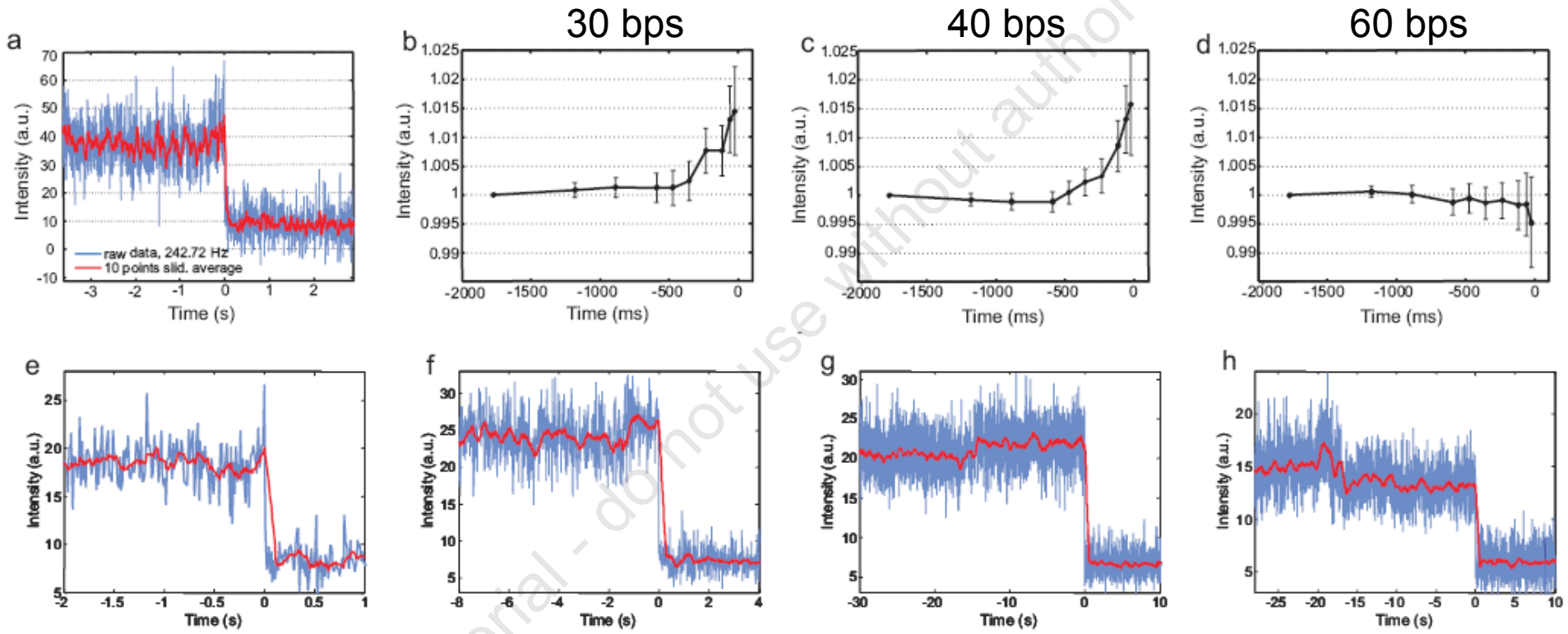
85 Hz

53 seconds

Several single molecule cutting trajectories



Statistical analysis of trajectories

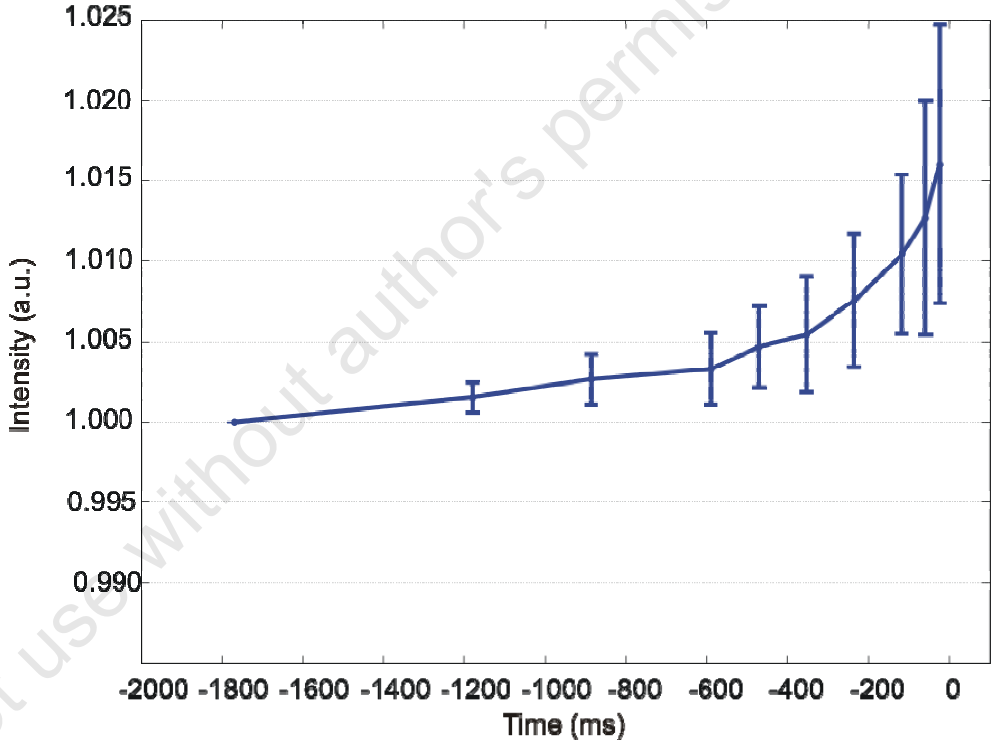


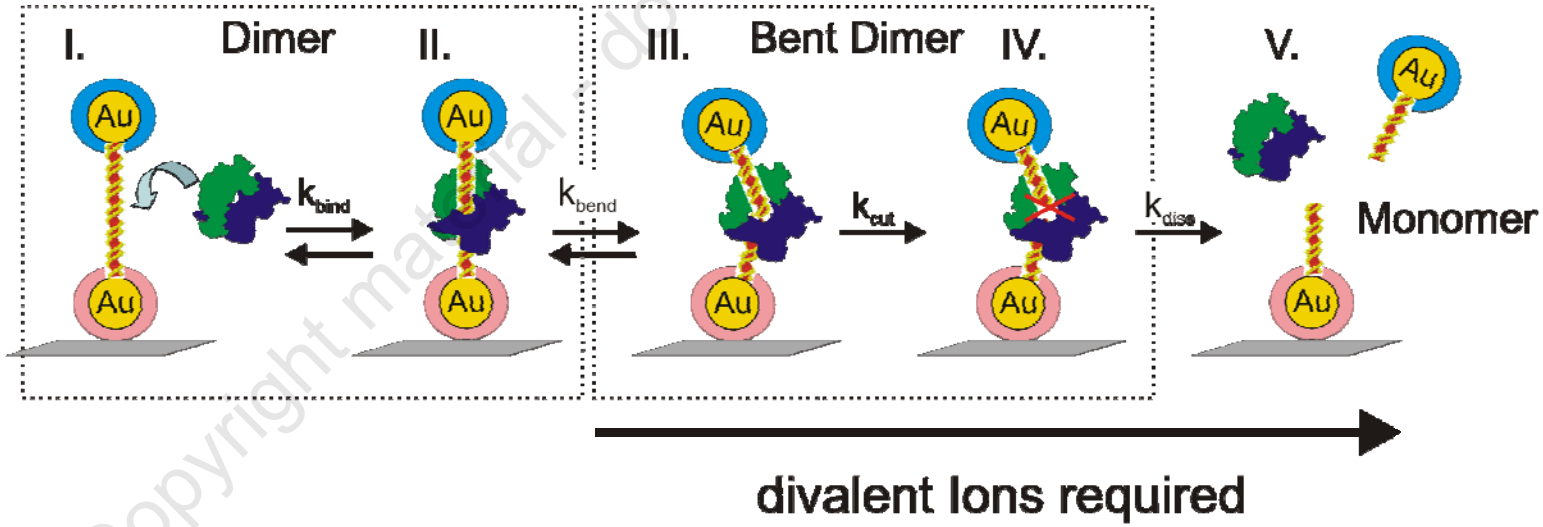
Enzyme binding does not account intensity increase before cut

a) Prebind EcoRV in the absence of Mg^{2+}

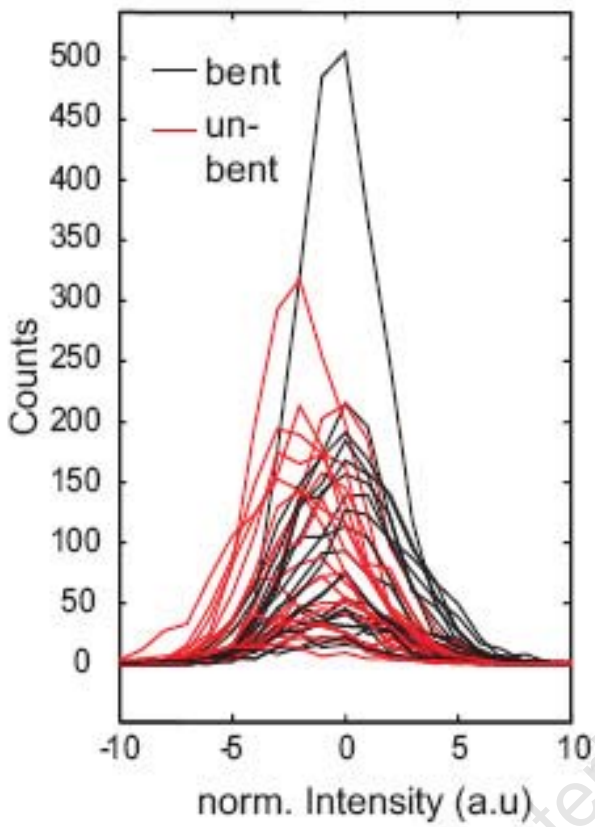
b) Remove excess Enzyme

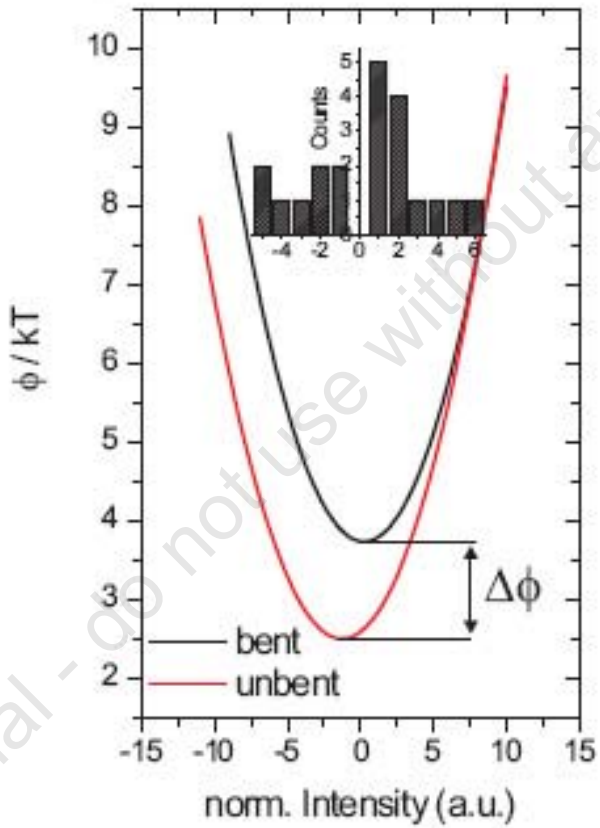
c) Add Mg^{2+}

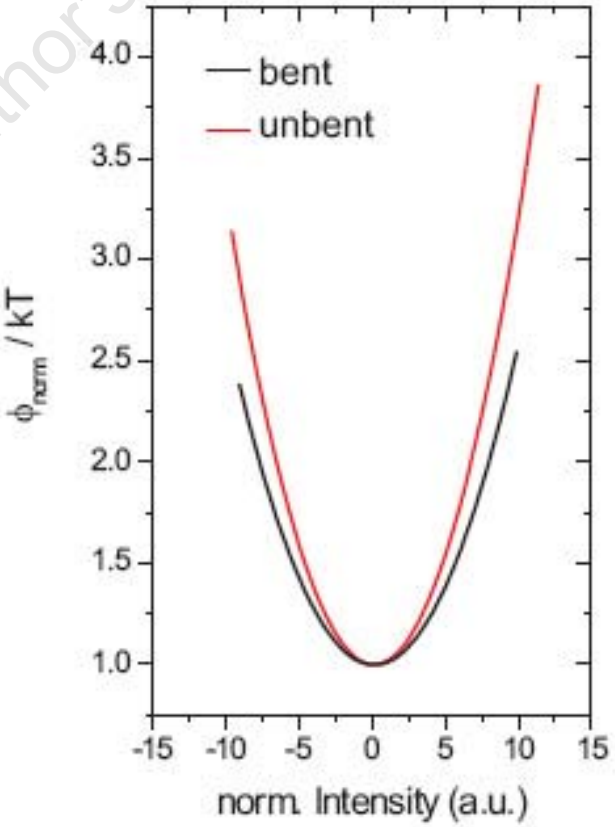




Interaction potential between the Au particles in the straight and unbent states



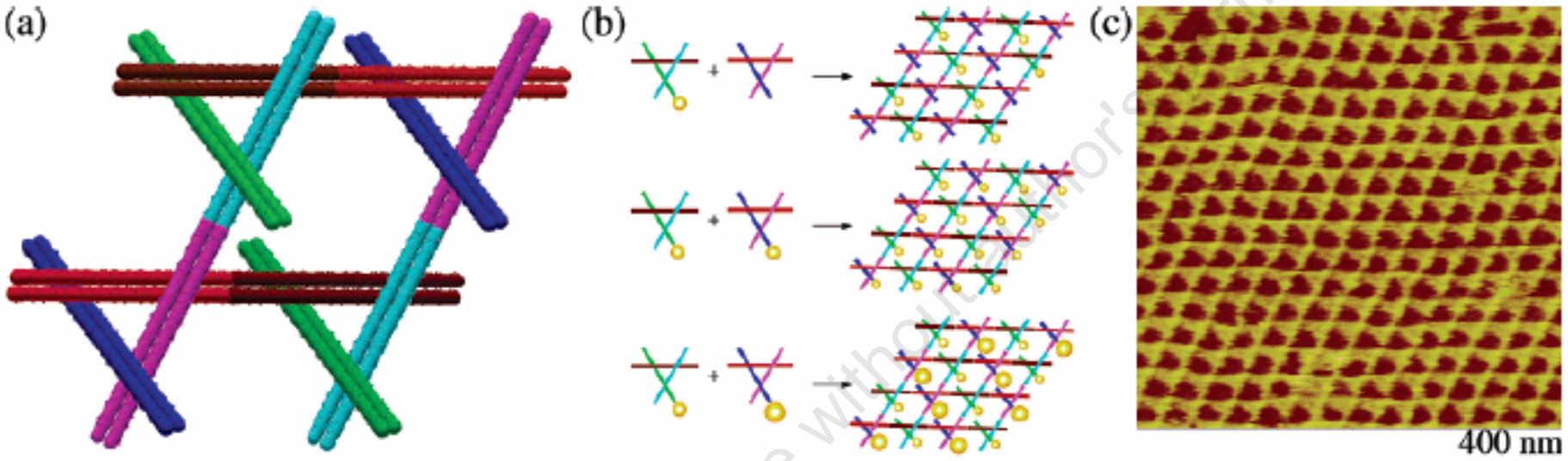


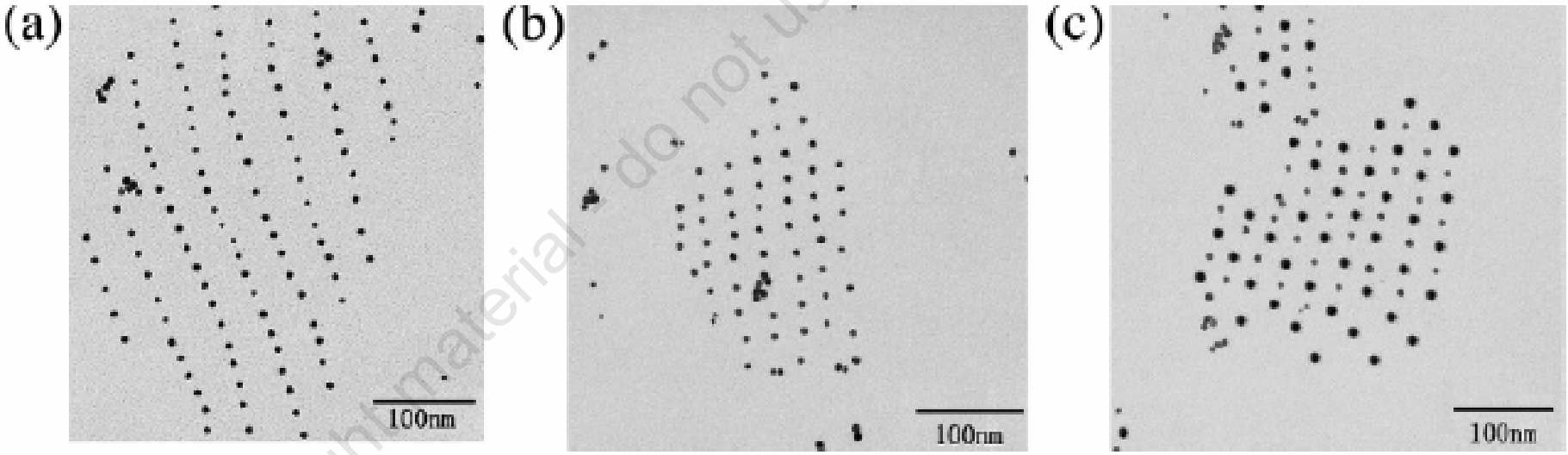


FRET vs. Plasmon Rulers

	FRET	**Plasmon Rulers**
Lifetime	For Cy3/Cy5 dye pair ~ 40 s	Hours to days
Blinking	Yes	No
Distance Dependence	$\sim 1/R^6$	$\sim e^{-R}$
Accessible Distances	1-10 nm	1-70 nm
Orientation dependence	Yes	No

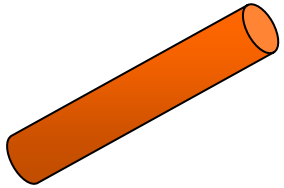
DNA tiles and nanocrystals



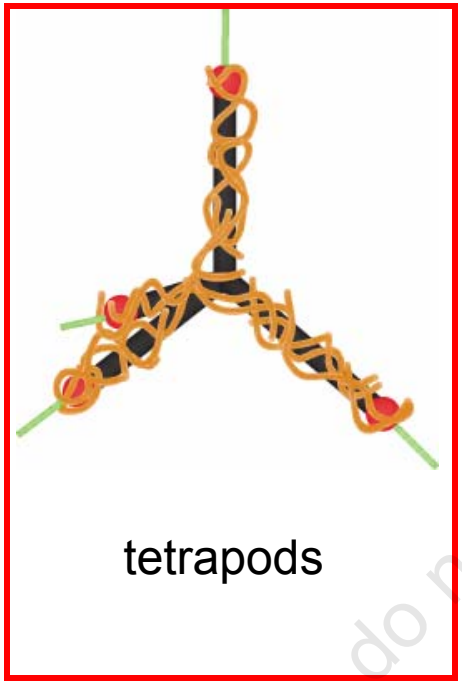


J. W. Zheng, P. E. Constantinou, C. Micheel, A. P. Alivisatos, R. A. Kiehl, and N. C. Seeman "Two-dimensional nanoparticle arrays show the organizational power of robust DNA motifs," Nano Letters **6**, 1502 (2006).

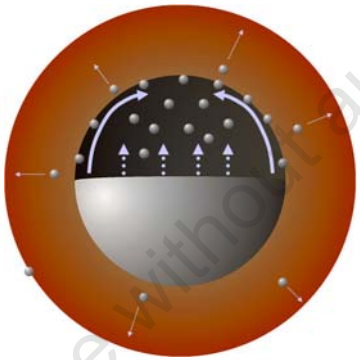
New nanocrystals for biological imaging applications



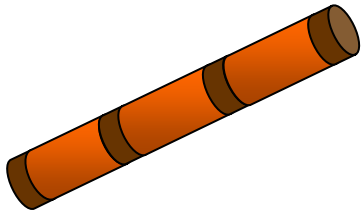
rods



tetrapods



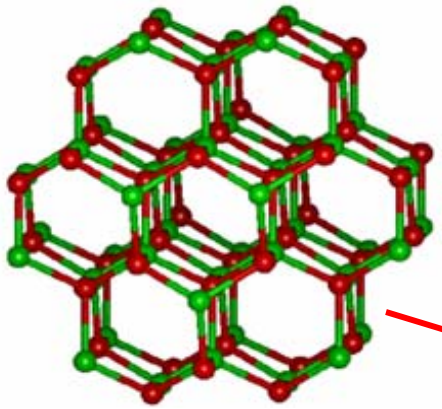
Hollow and nested



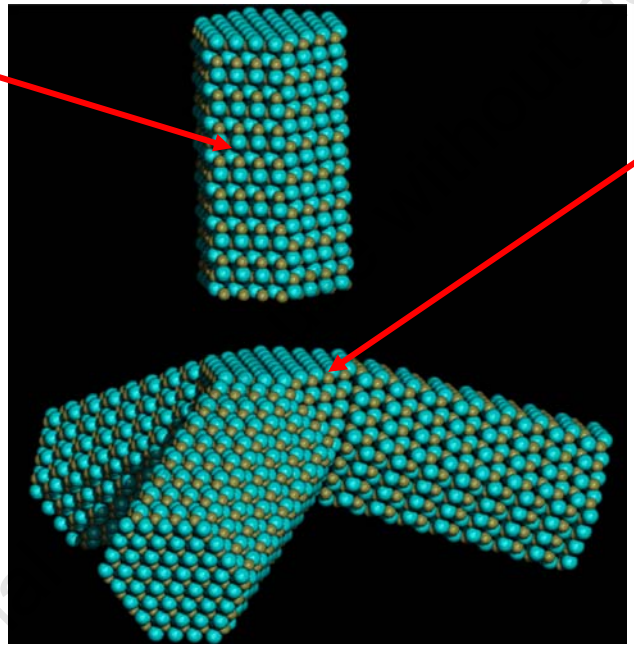
striped

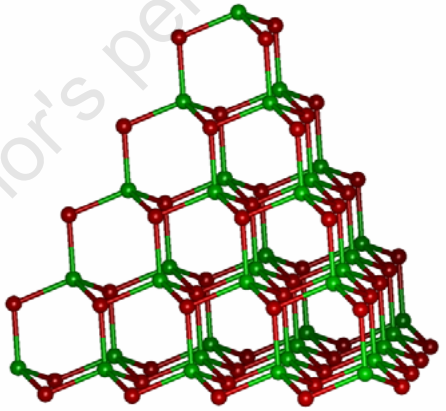
Shelley Claridge
Charina Choi

Wurtzite and Zinc Blende polytypism
a mechanism for branching II-VI nanocrystals



WZ
Stabilized by
surfactant
Growth in WZ



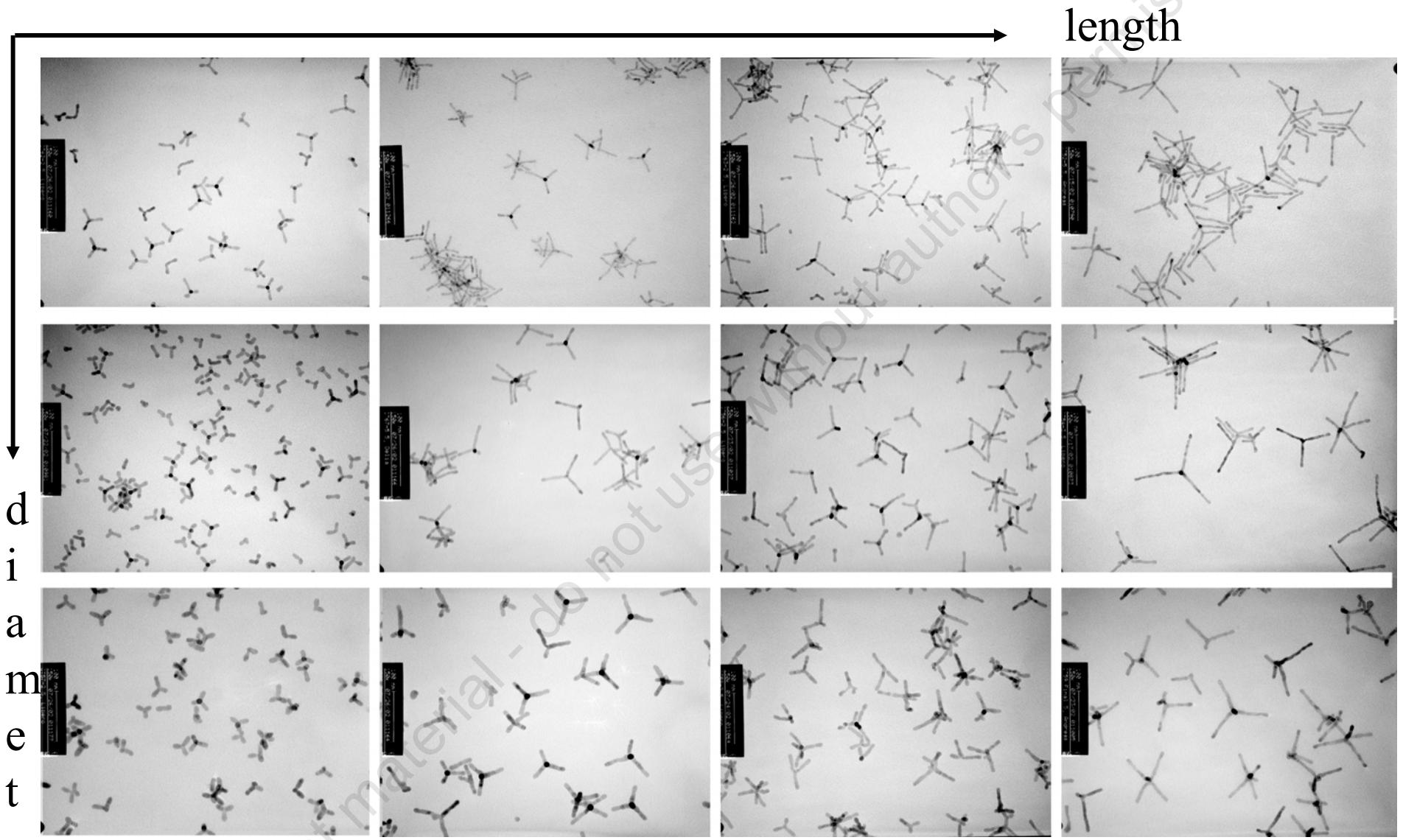


ZB
More stable
by 7meV/unit cell
nucleation in ZB

Manna, L., E. C. Scher, et al. (2000). "Synthesis of soluble and processable rod-, arrow-, teardrop-, and tetrapod-shaped CdSe nanocrystals." Journal of the American Chemical Society **122**(51): 12700-12706.

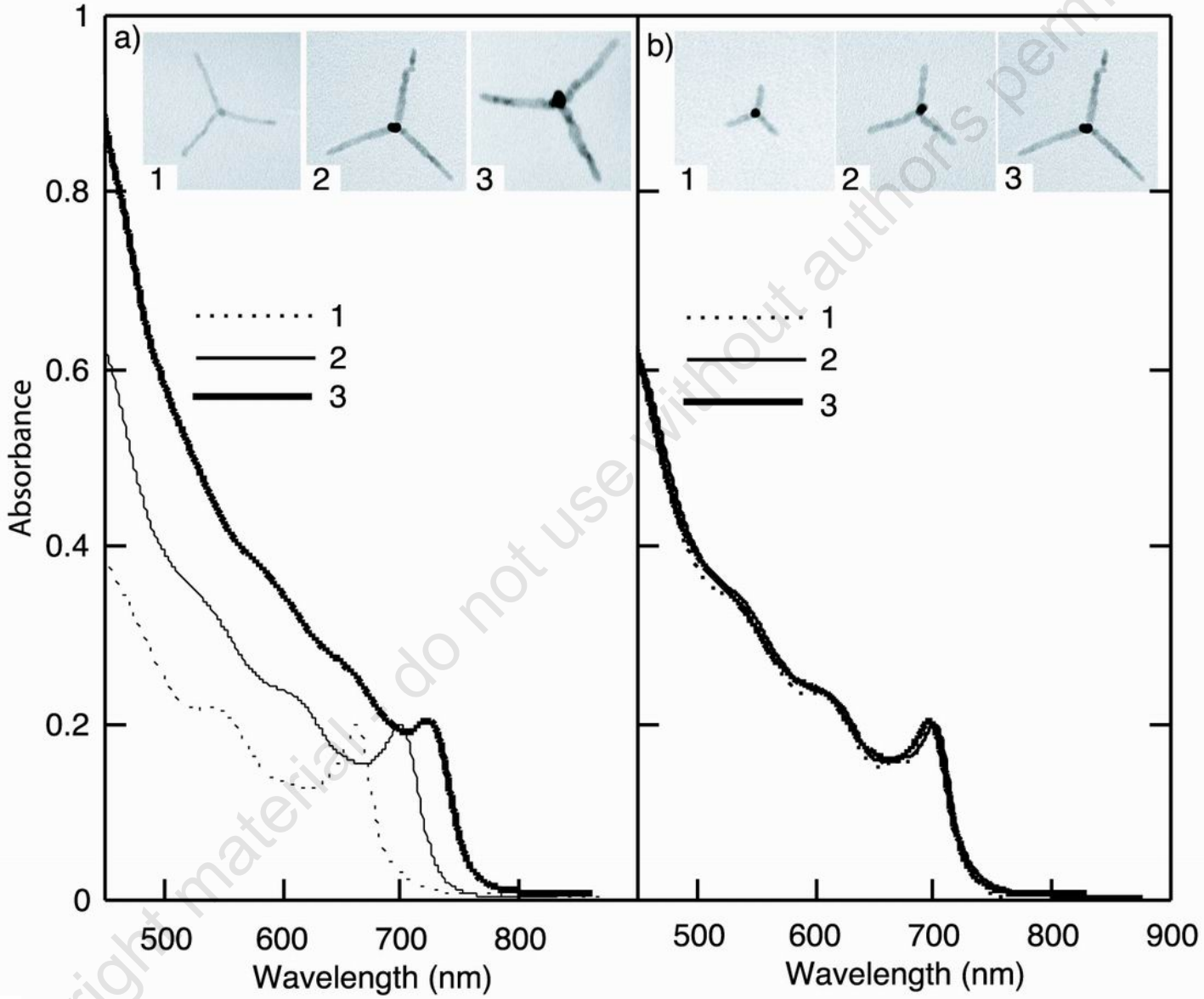
Manna, L., D. J. Milliron, et al. (2003). "Controlled growth of tetrapod-branched inorganic nanocrystals." Nature Materials **2**(6): 382-385.

CdTe Tetrapods

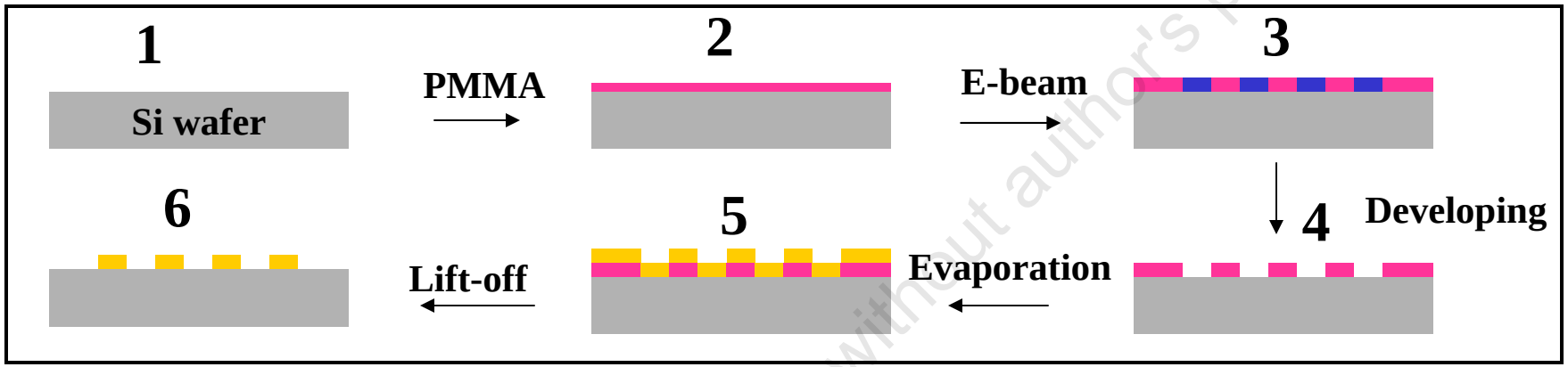


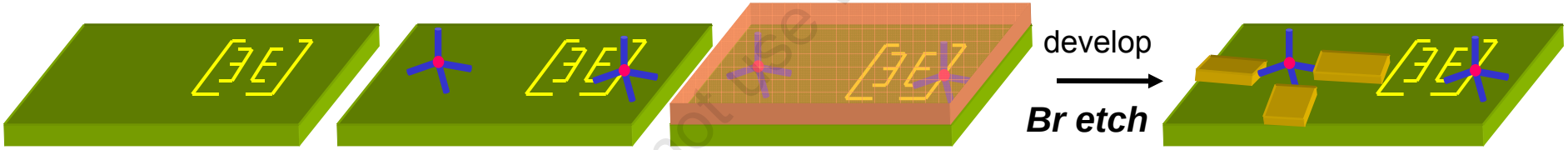
Manna, L., D. J. Milliron, A. Meisel, E. C. Scher and A. P. Alivisatos
"Controlled growth of tetrapod-branched inorganic nanocrystals." Nature Materials 2(6): 382-385. (2003).

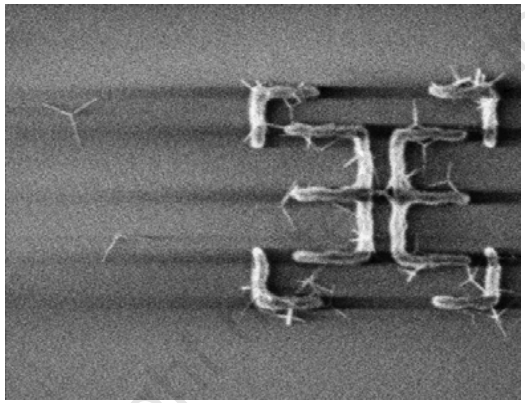
Quantum Confinement in Tetrapods

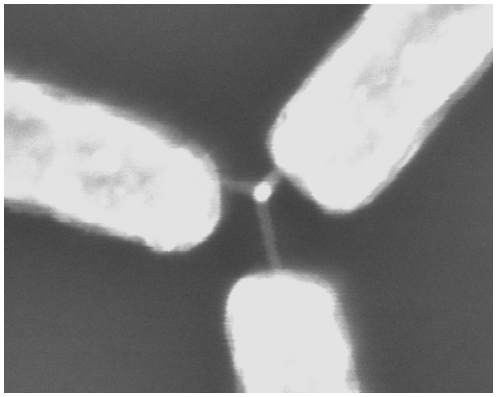


E-beam, alignment, etch and contact



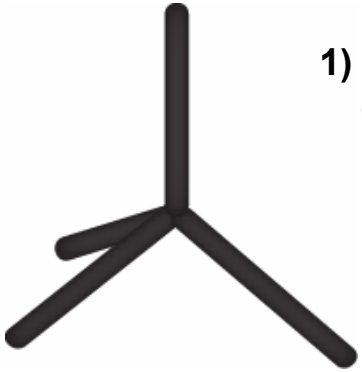




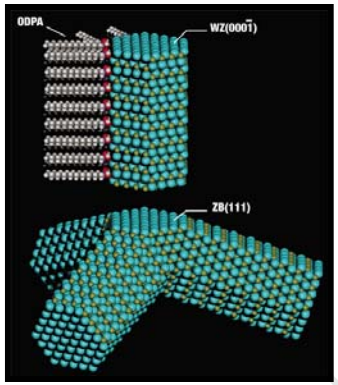


20 nm alignment accuracy in e-beam lithography.

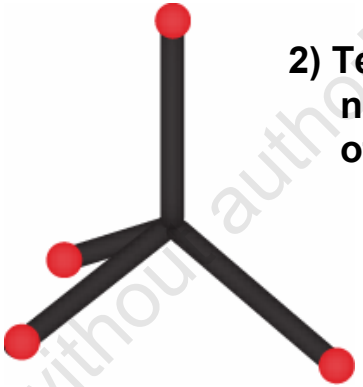
Route to Biofunctionalized Tetrapods



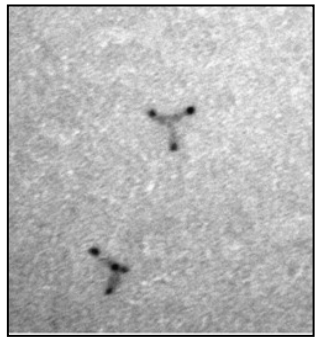
1) Solution-phase synthesis of tetrapods



Manna *et al.*, *Nature Mater.*, **2003**, *2*, 382.



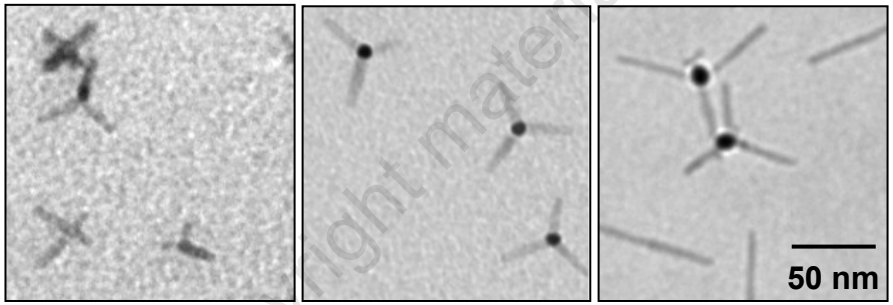
2) Tetrapod tips provide nucleation sites for formation of gold nanoparticles

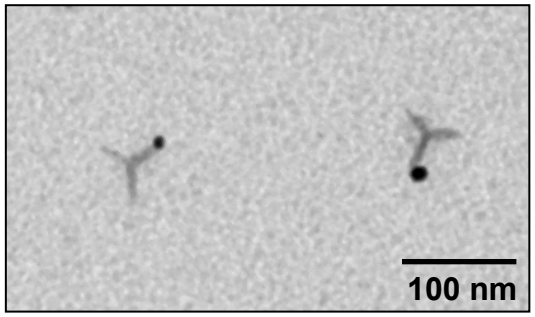


Mokari *et al.*, *Science*, **2004**, *304*, 1787.

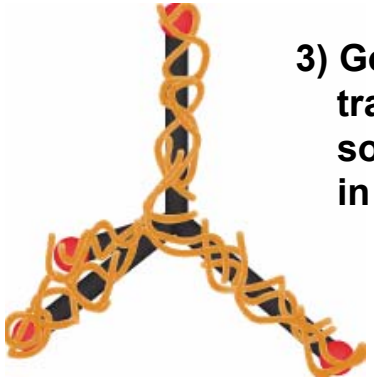
Cd/S ratio

1:1 **2:1** **4:1**

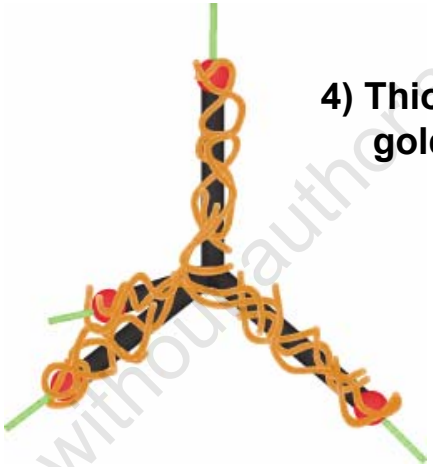




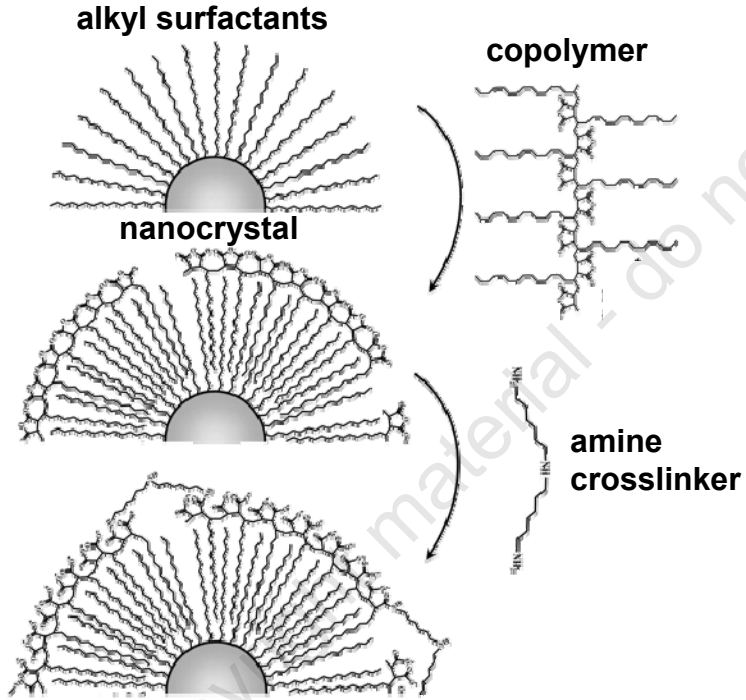
Route to Biofunctionalized Tetrapods

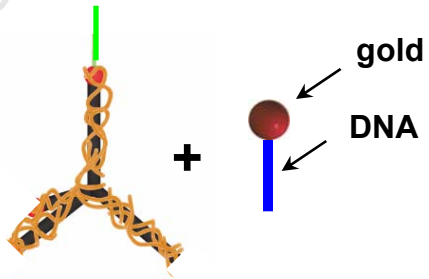


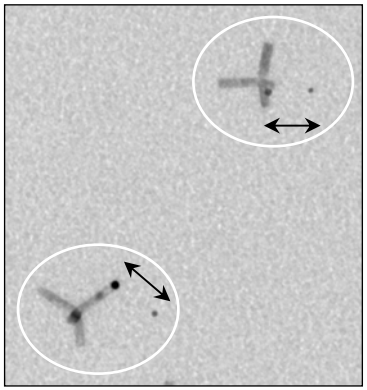
3) Gold-tipped tetrapods are transferred from organic solvent to water by wrapping in amphiphilic copolymer

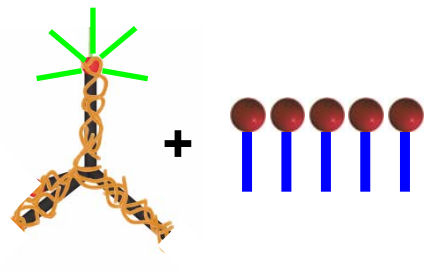


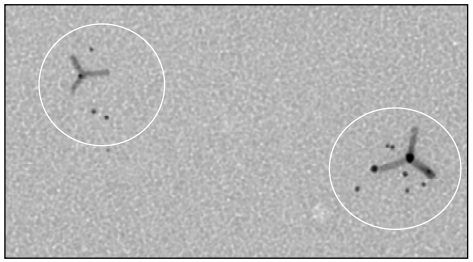
4) Thiolated DNA attached to gold tips





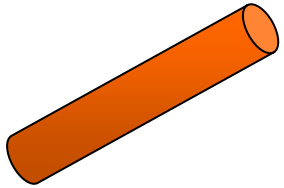




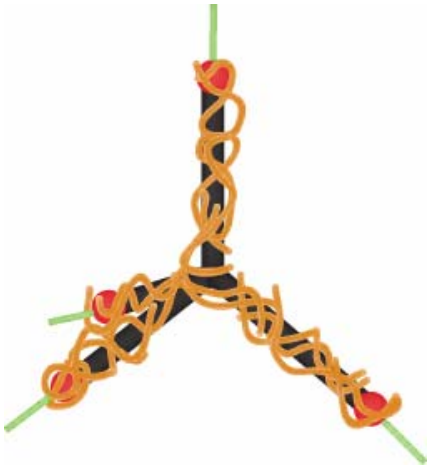


Pellegrino *et al.*, *Nano Lett.*, **2004**, *4*, 703.

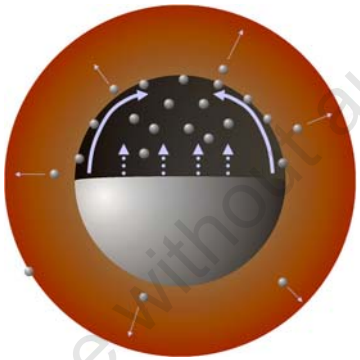
New nanocrystals for biological imaging applications



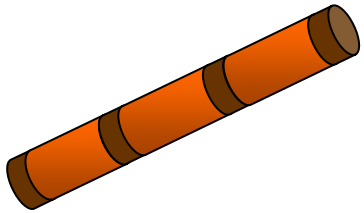
rods



tetrapods



Hollow and nested

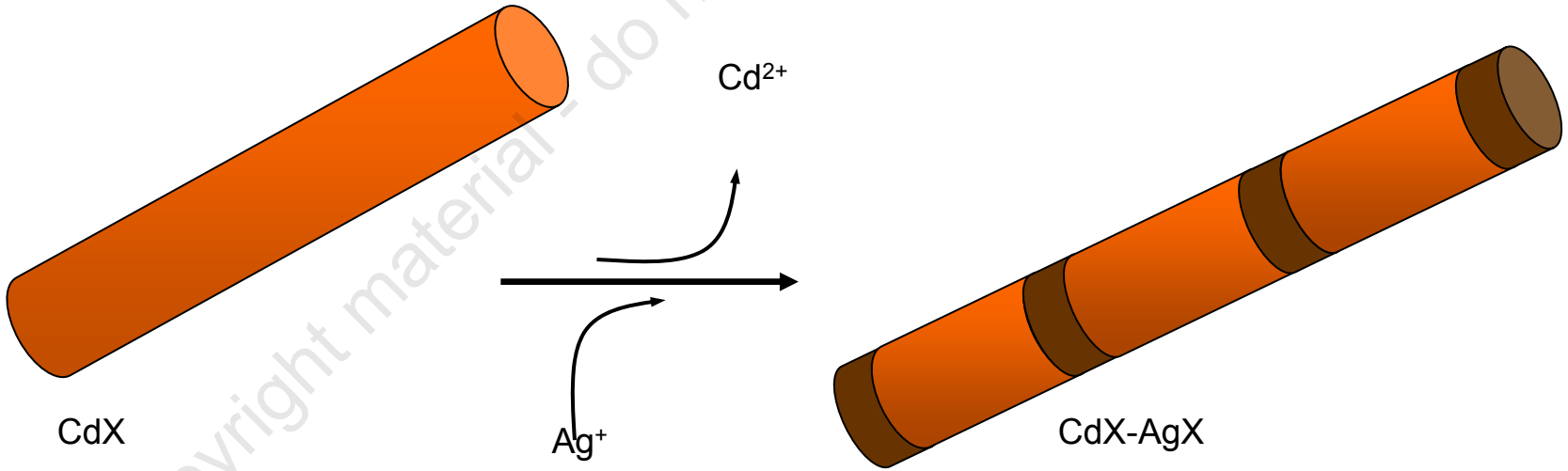


striped

Rich Robinson
Bryce Sadtler

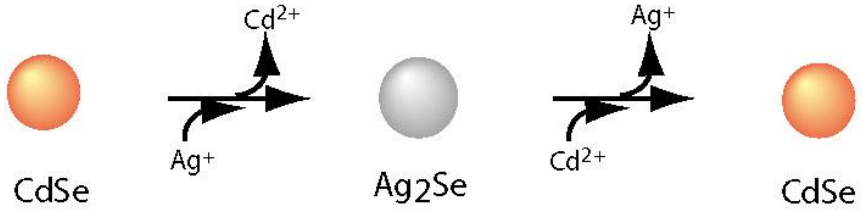
Partial Cation Exchange in Colloidal Nanocrystals

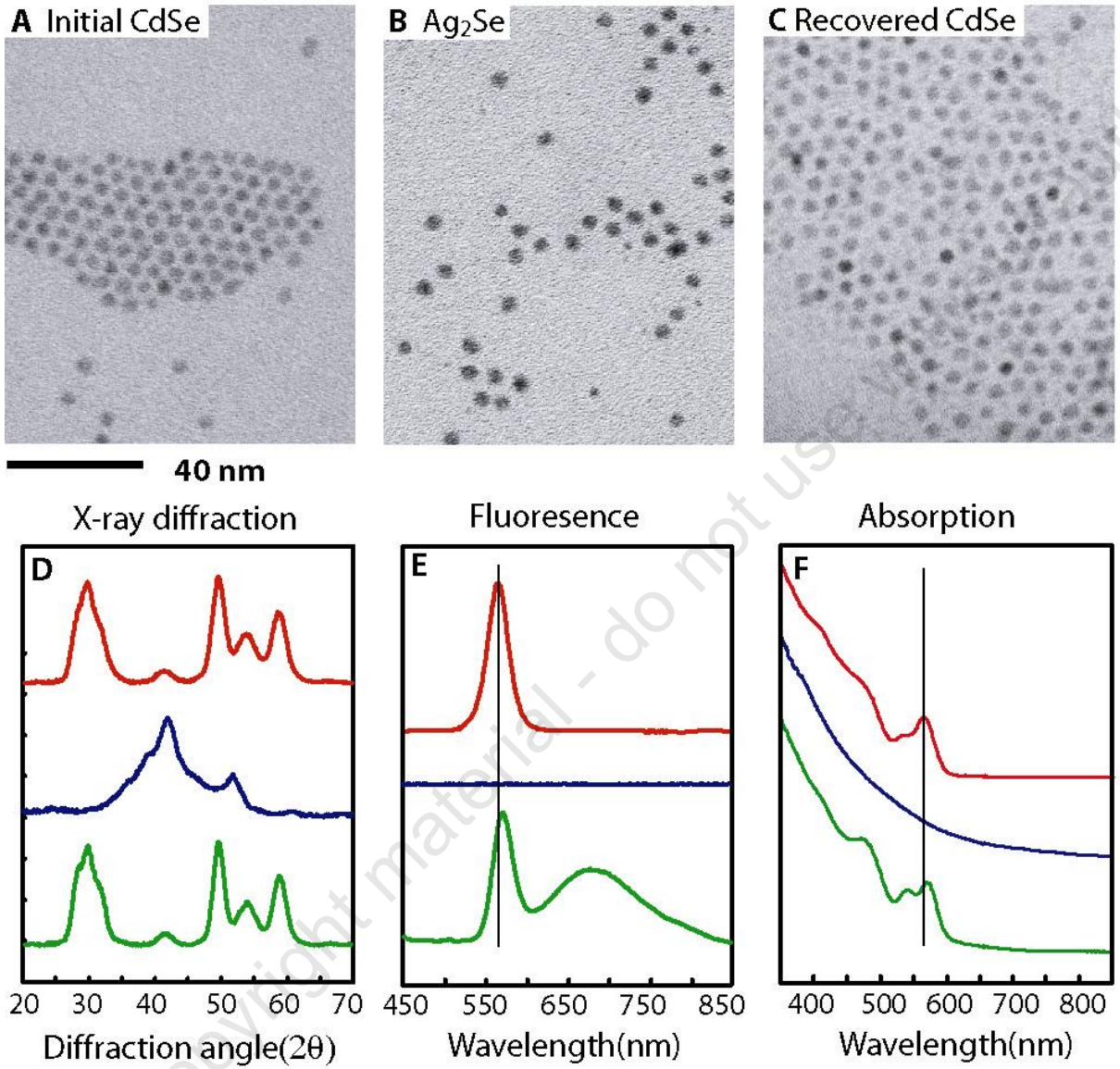
Previous work on complete exchange:
Dong Hee Son, Steven M. Hughes, Yadong Yin, and A. P. Alivisatos
Science 306 1009 (2004)

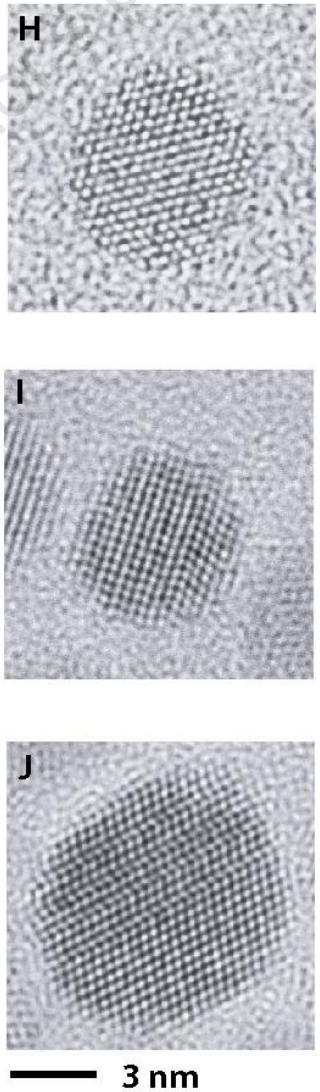


(X = S, Se)

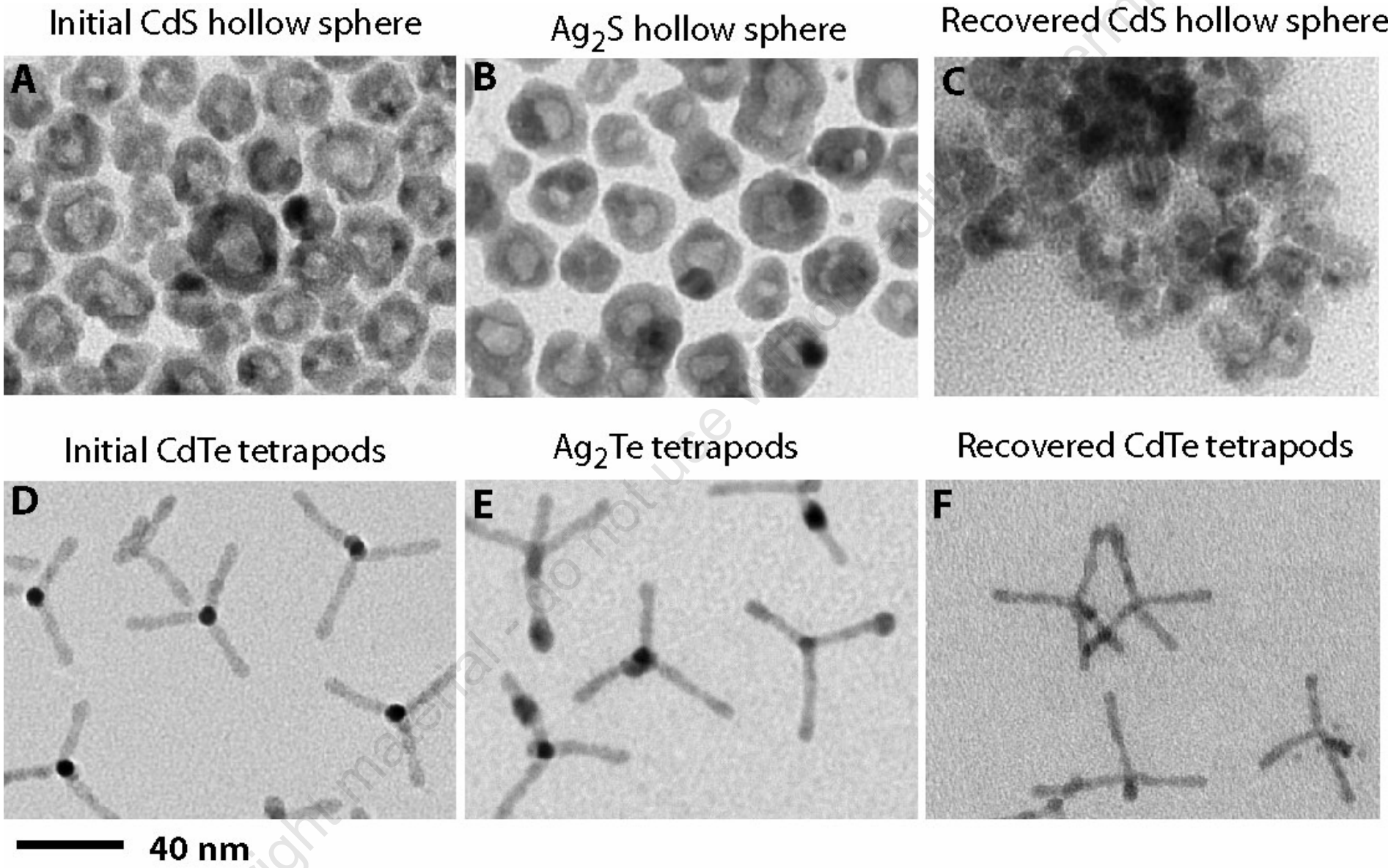
Cation Exchange





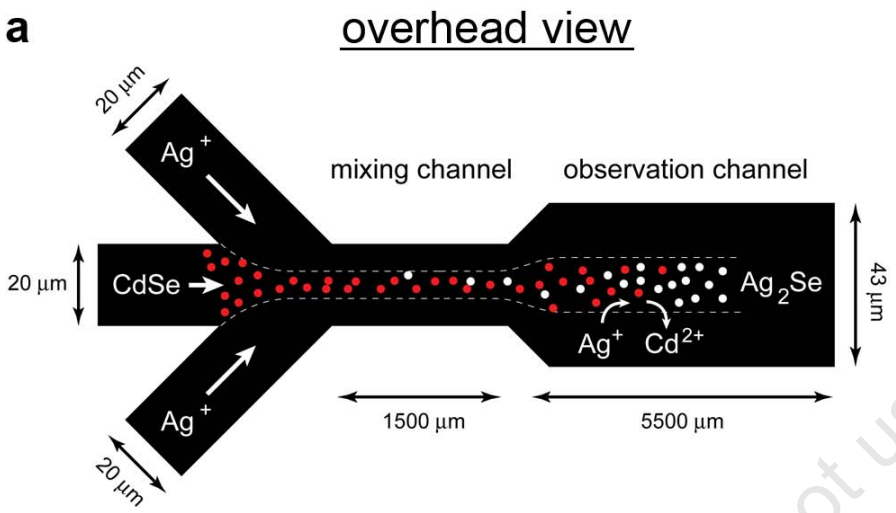


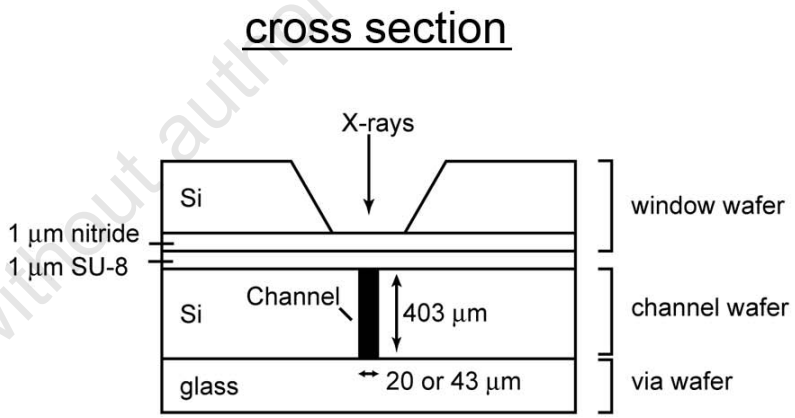
Cation exchange cycles in complex nanostructures

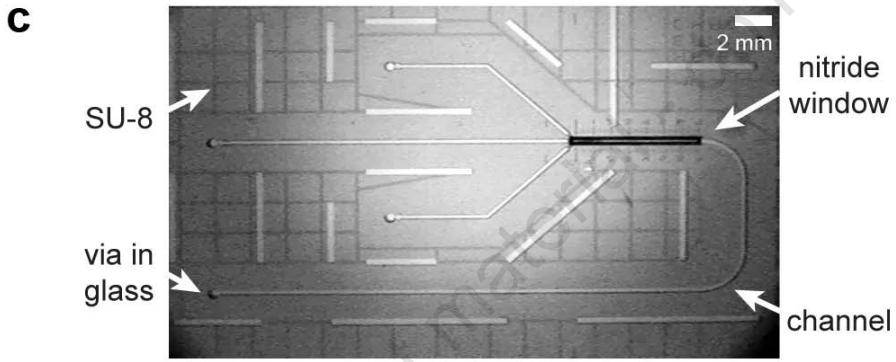


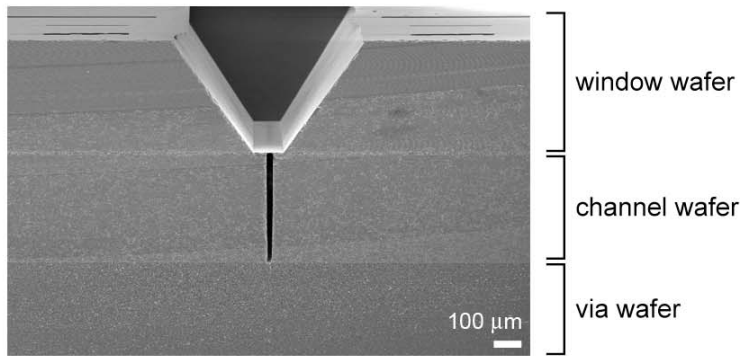
Sequential operations in nanocrystal synthesis

Cation Exchange Microfludic Kinetic Measurements





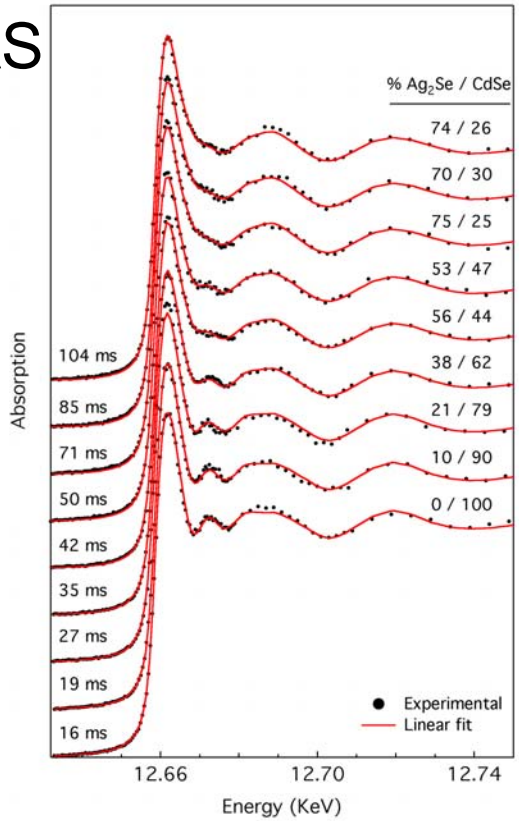




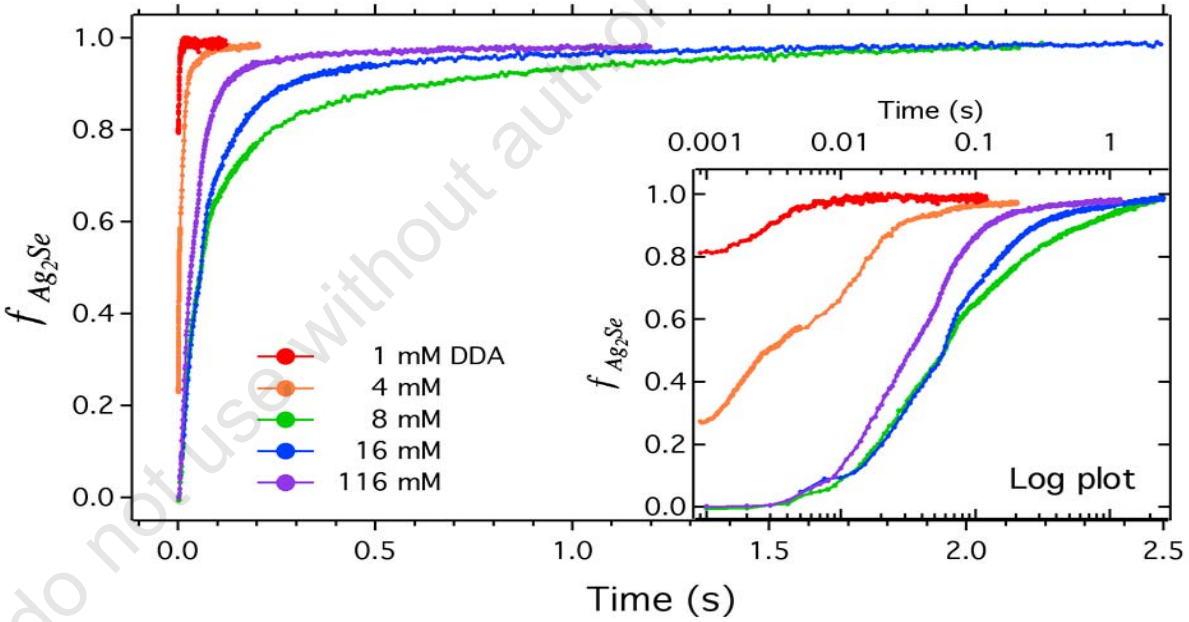
Emory Chan and Prof. R. Mathies

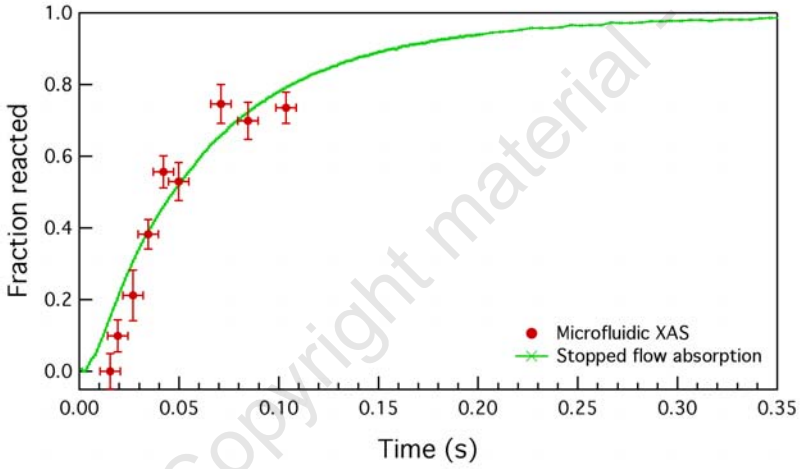
Cation Exchange Kinetics

XAS



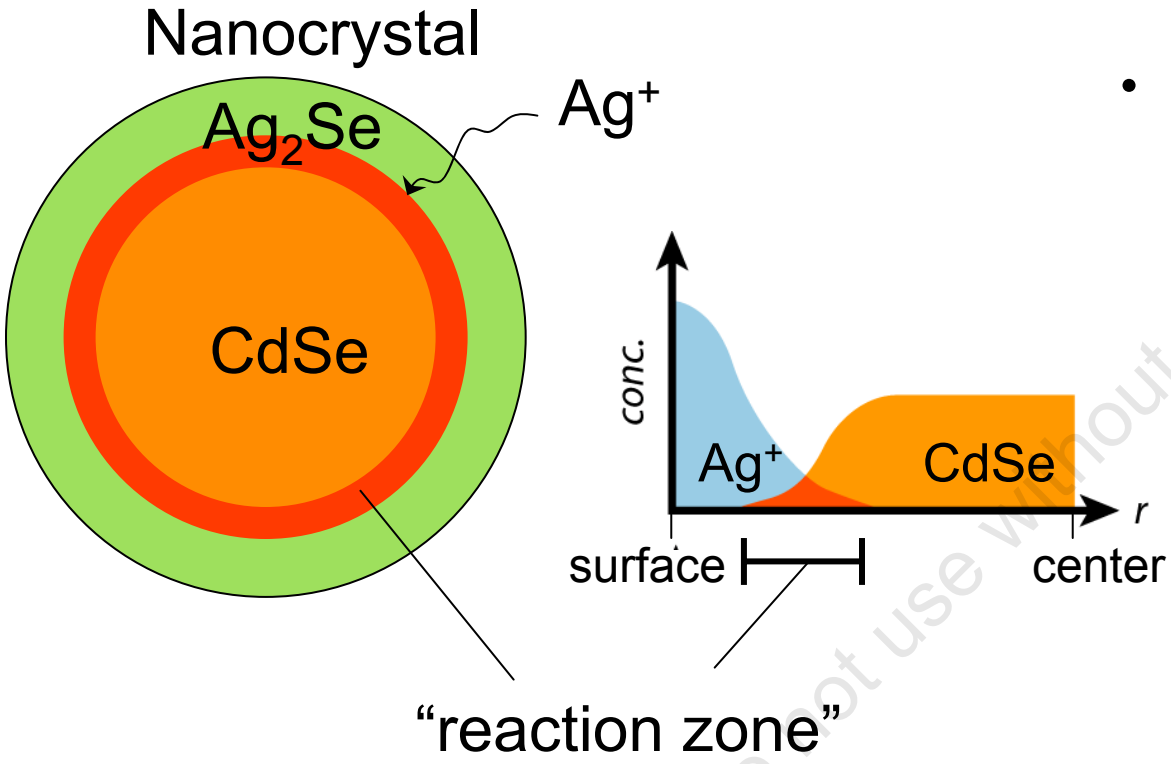
stopped flow visible absorption





Emory Chan, Matthew Marcus,
Prof. R. A. Mathies

Time scale of cation exchange



- A spherical diffusion model can be used to extract the *effective* diffusion constant of Ag^+ in Ag_2Se/CdSe.
  - $D_{eff} = 5 \times 10^{14}$ cm^2/s

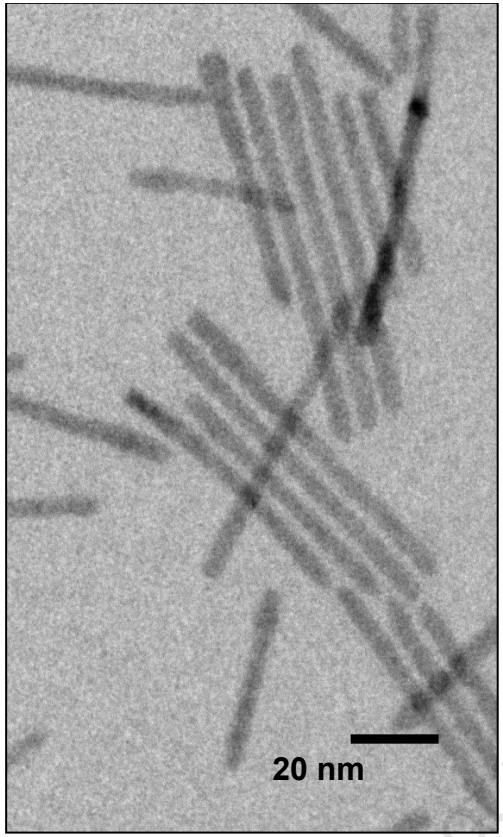
agrees with literature.

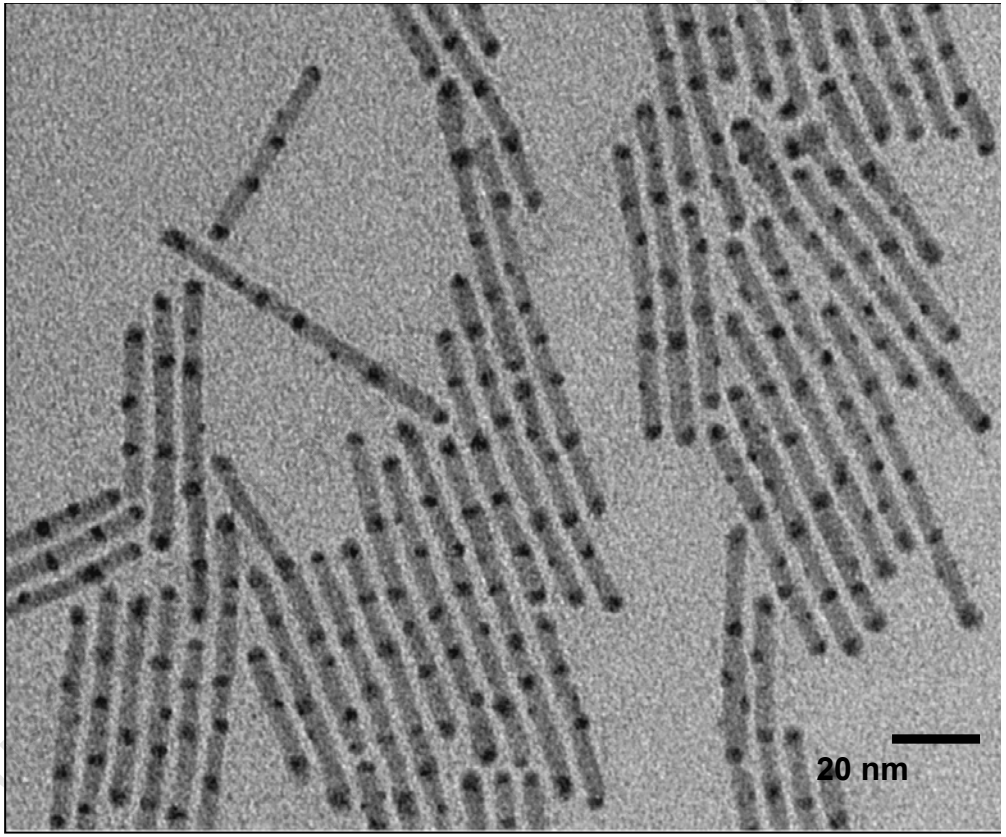
  - $D = 3 \times 10^{14}$ cm^2/s
  - $AgNO_3$ cation exchange on bulk CdSe (001) surface.
  - Leung *et al*, *J. Phys. Chem. 1991*, 95, 5918)

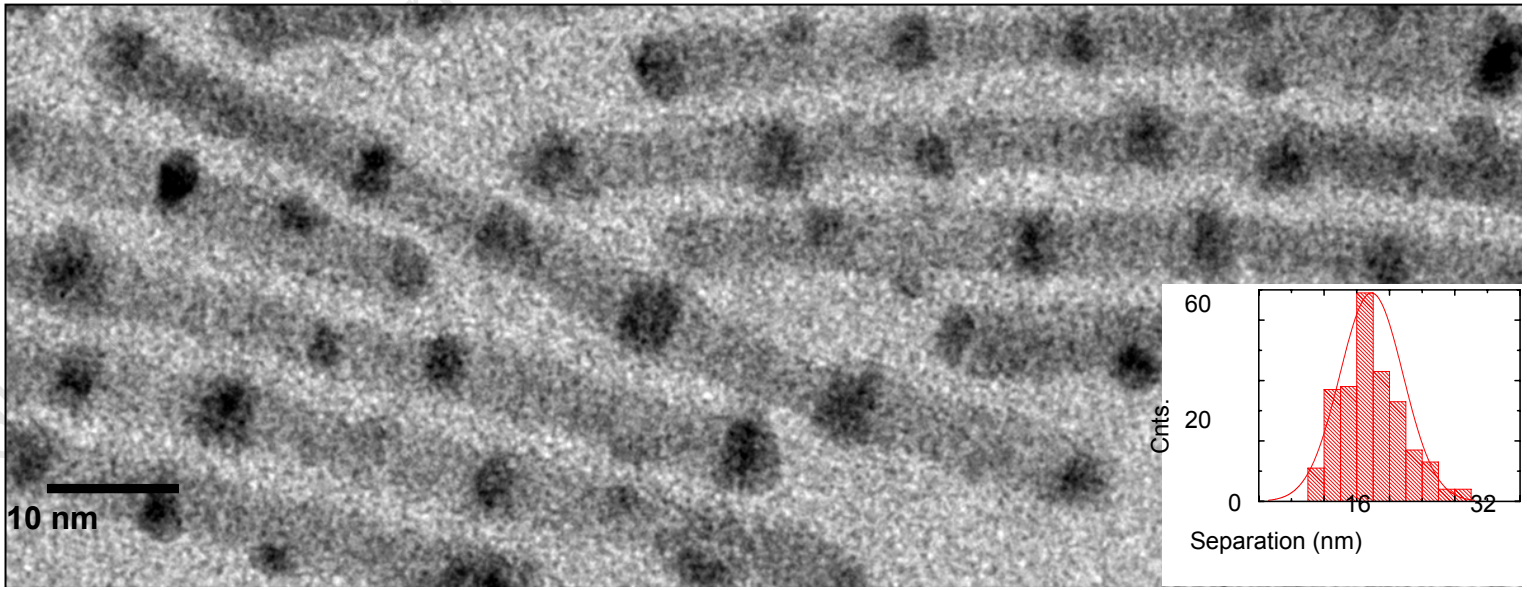
- $1/e = 66$ ms ~ 100 ms
- 4×10^7 collisions / second, between Ag^+, nanocrystals
- ~10^4 collisions result in 1 Ag_2Se molecule.
- Most reactions require 10^7-10^{11}

Partial Exchange?

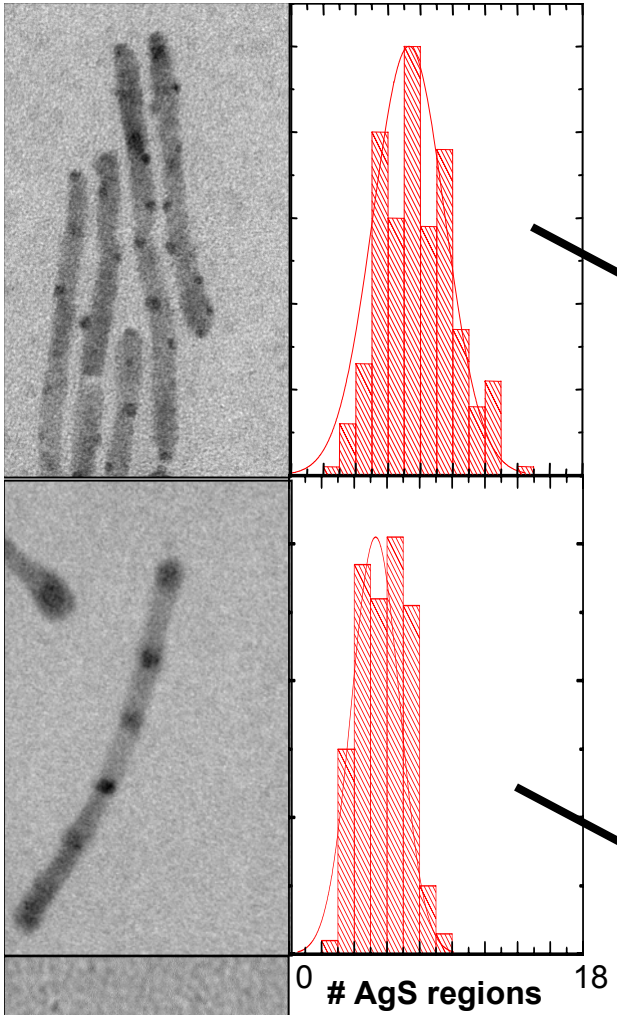
Partial cation exchange in nanorods

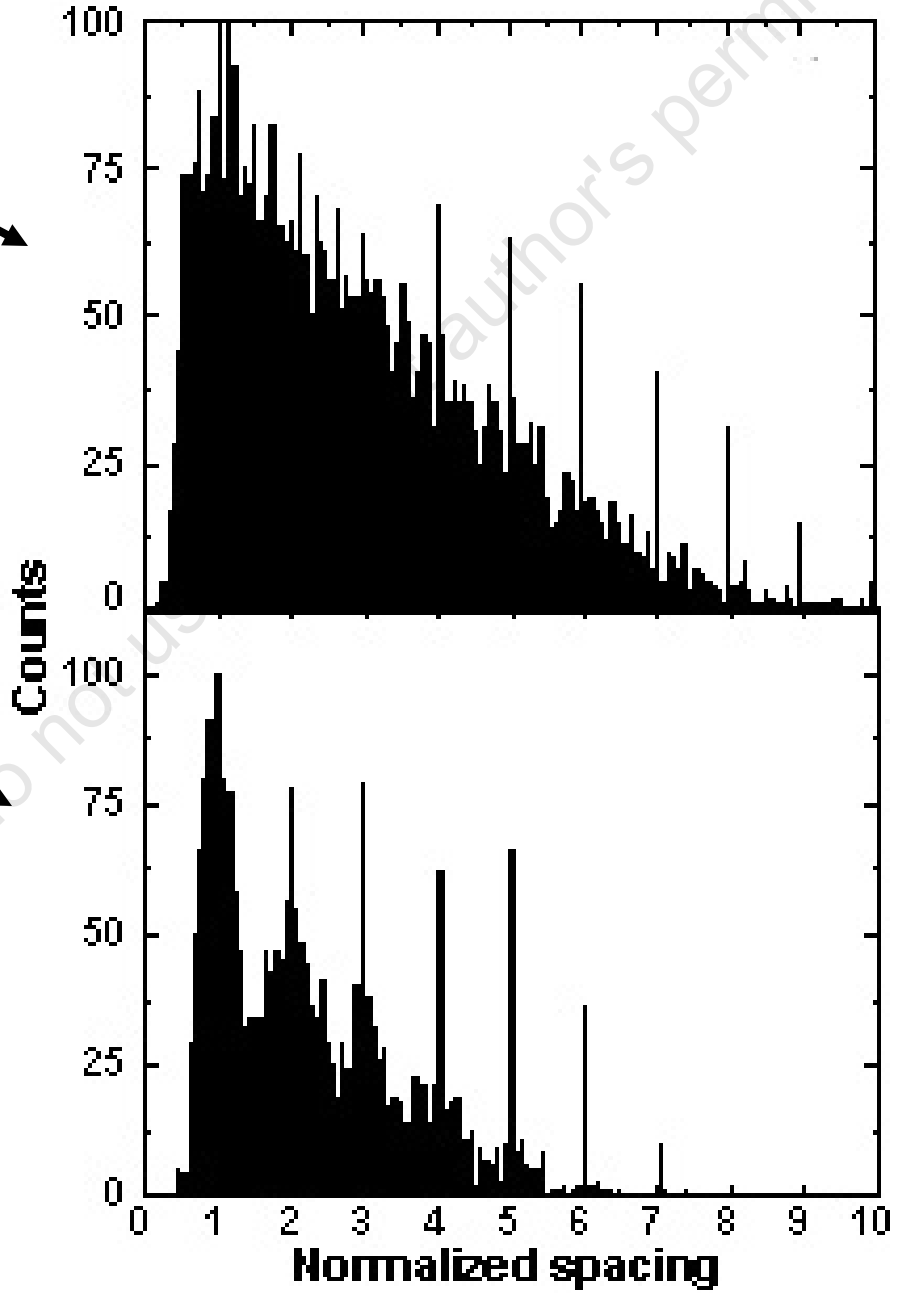




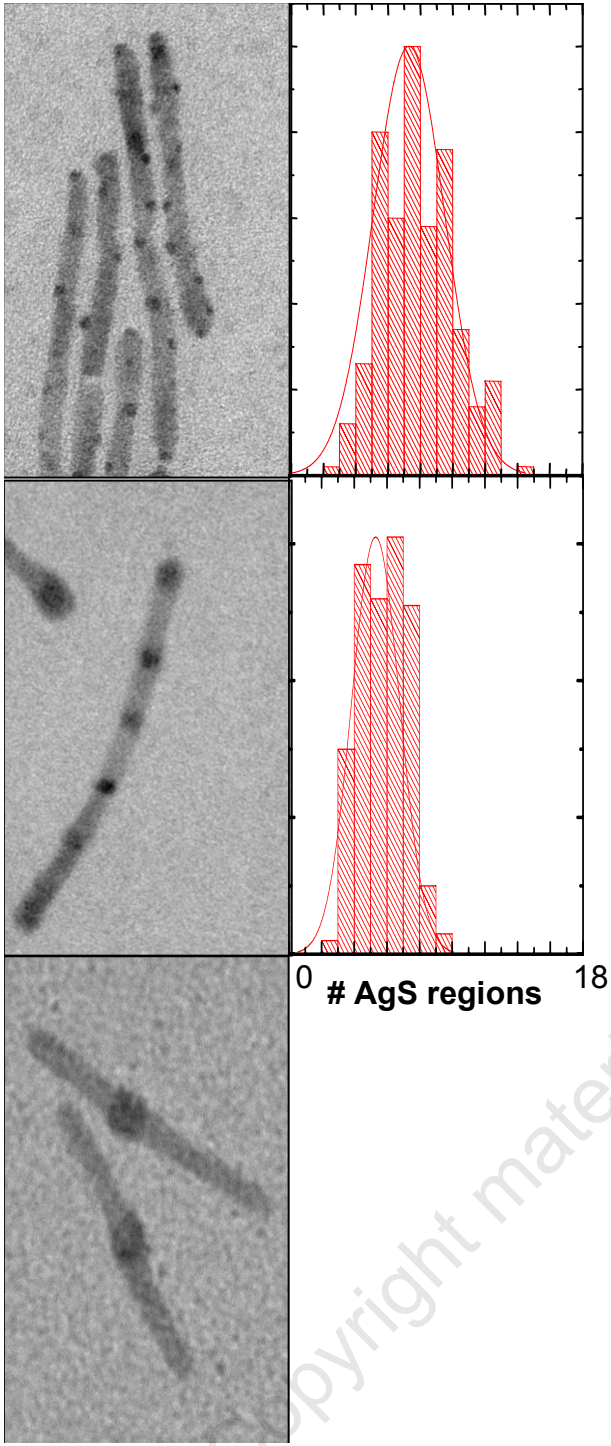


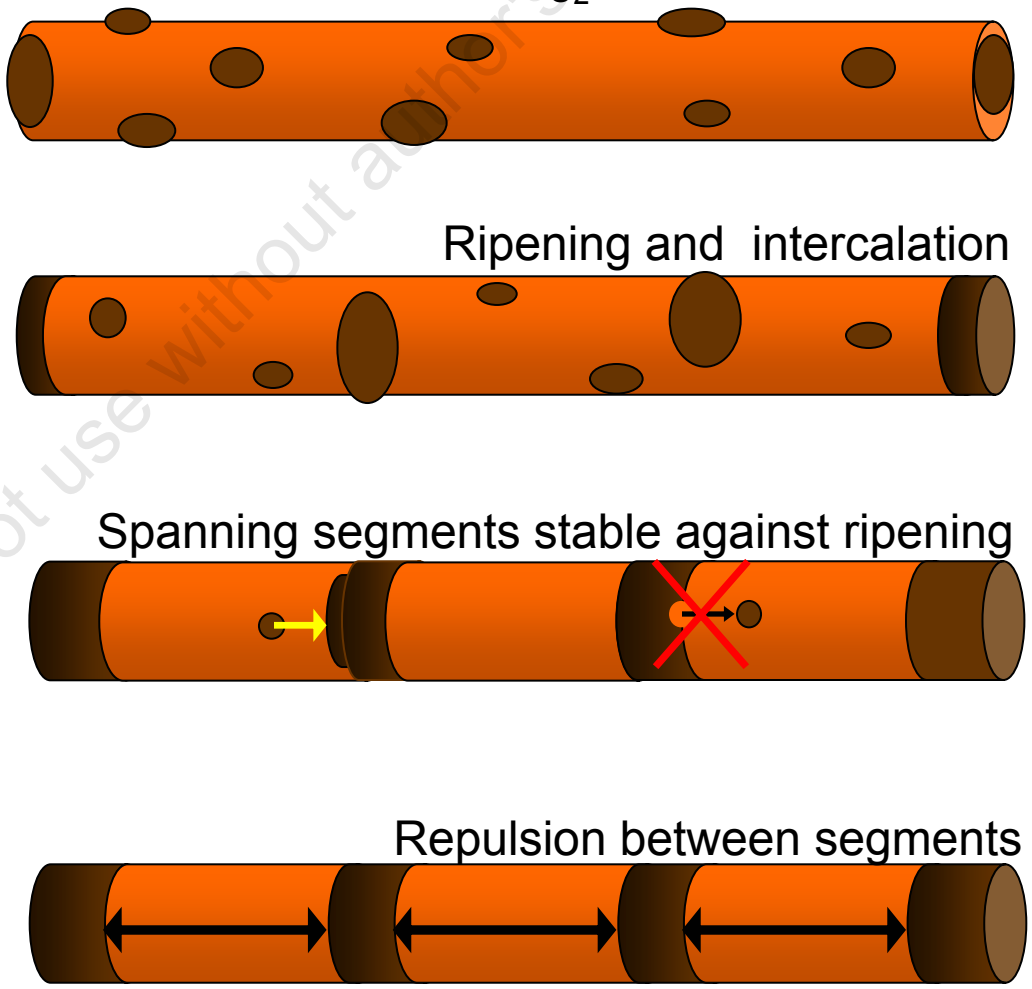
Evolution of the spaced dots in a rod



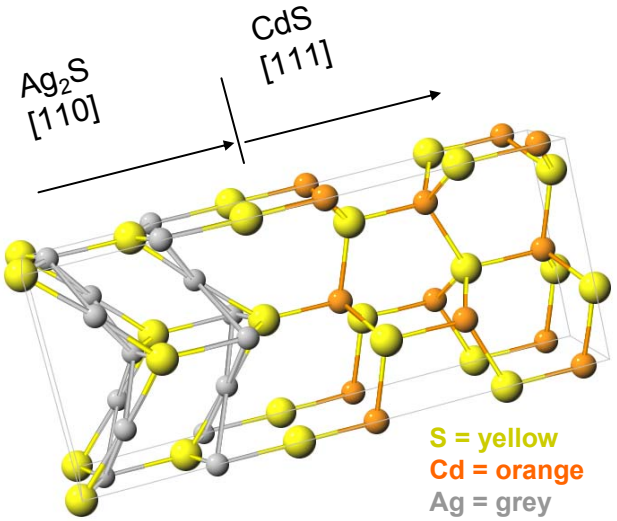


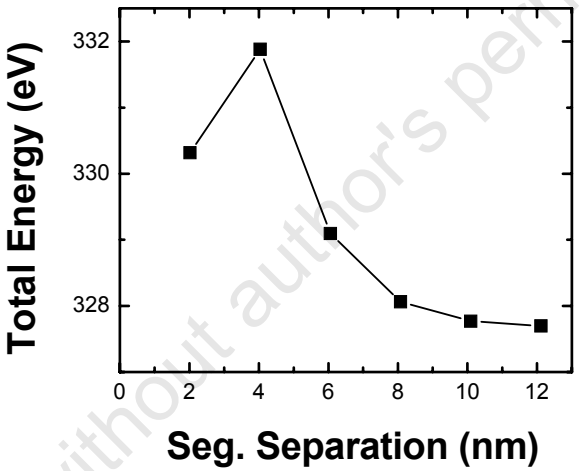
Evolution of the spaced dots in a rod

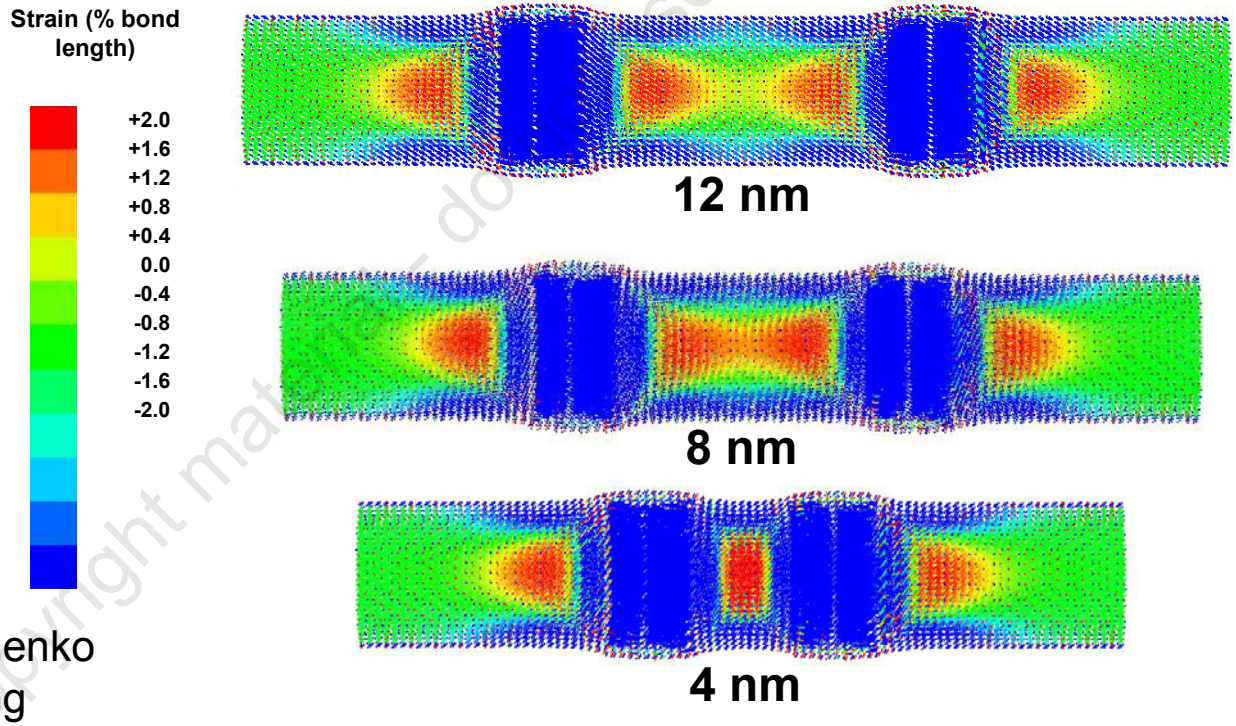




Strain model explains spacings

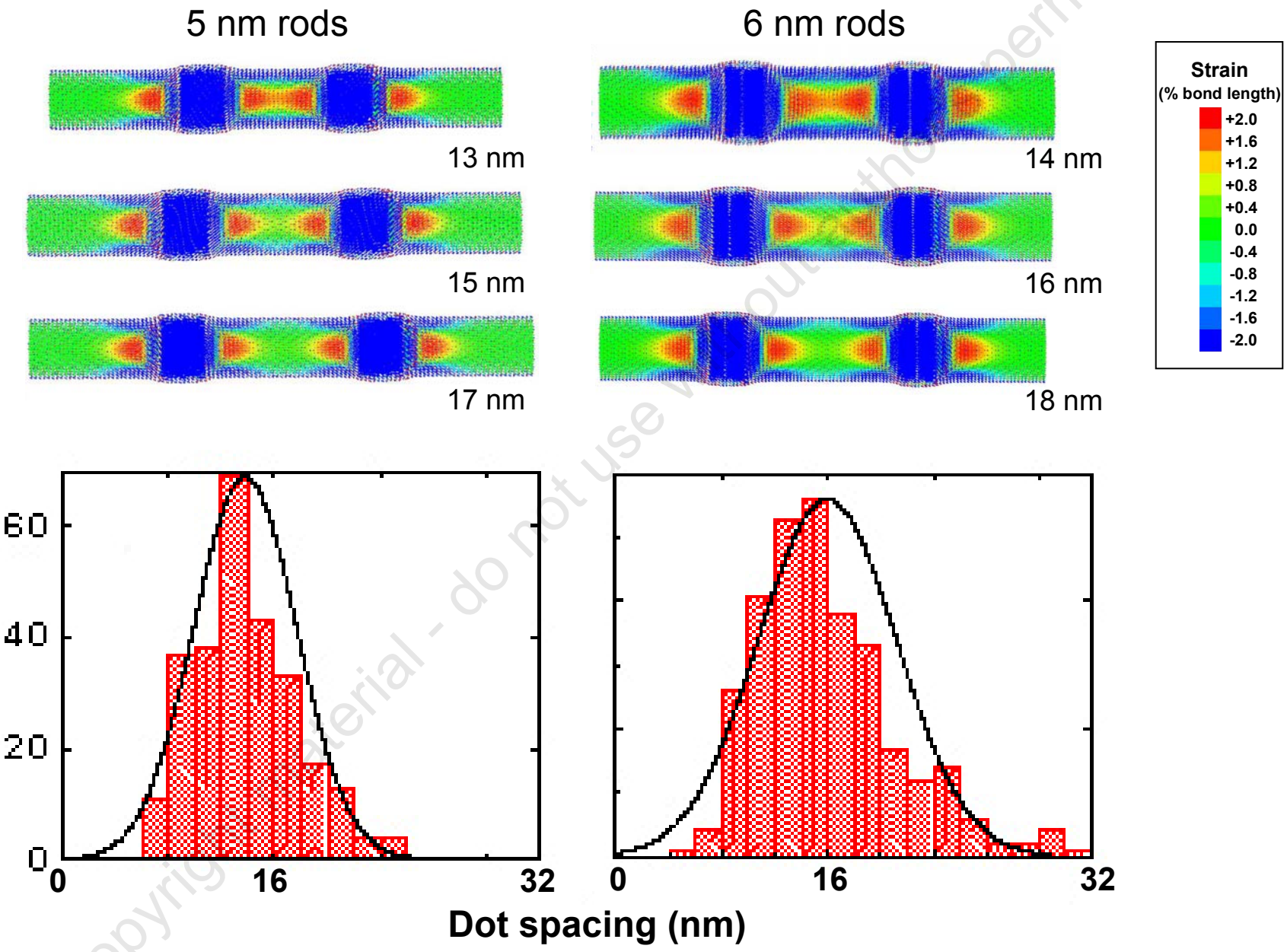




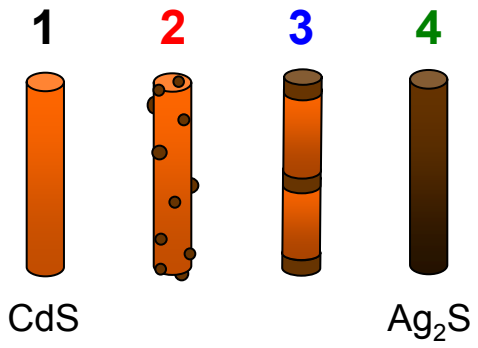


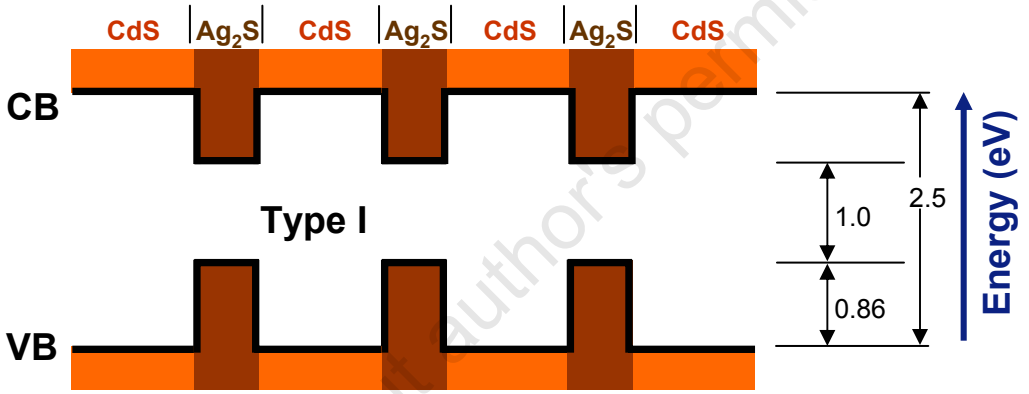
Dennis Demchenko
Lin Wang Wang

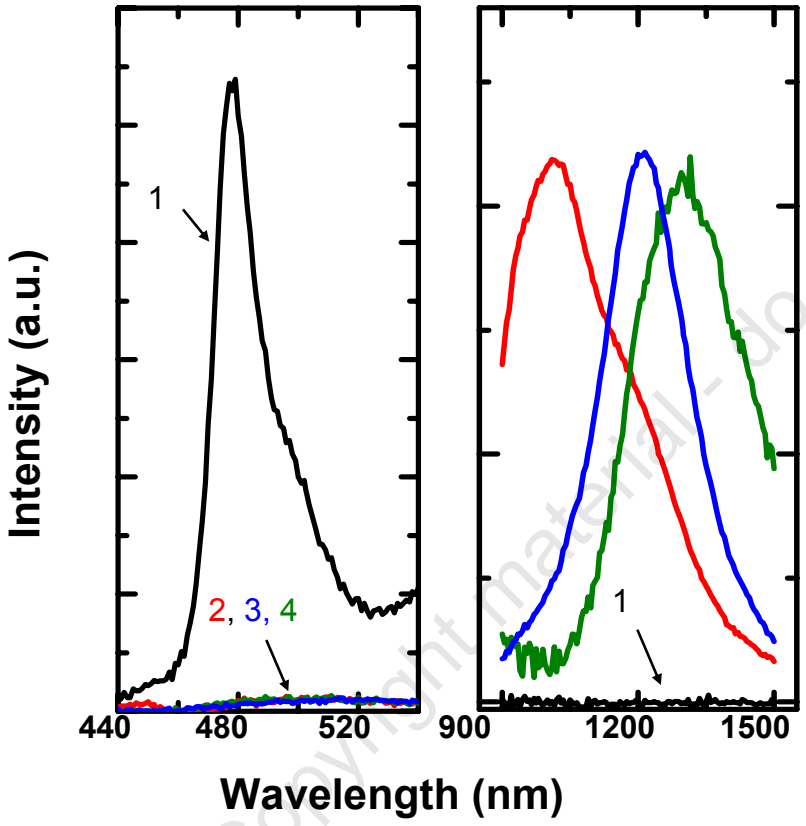
Diameter dependence of island spacings

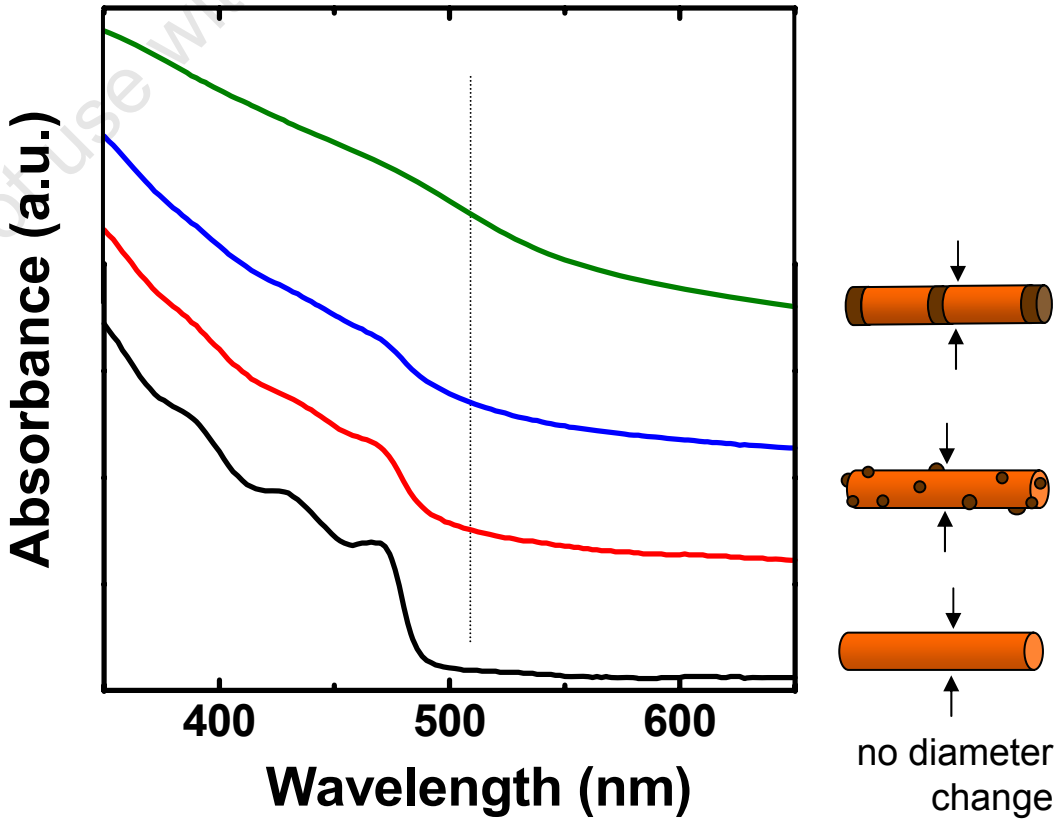


Optical properties and band offsets of partially exchanged rods

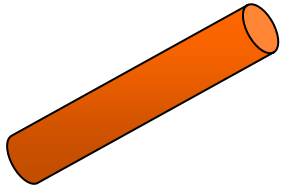




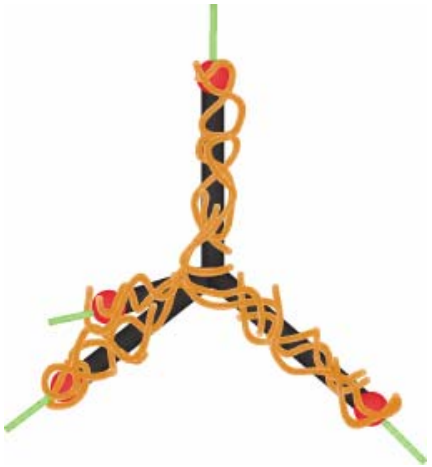




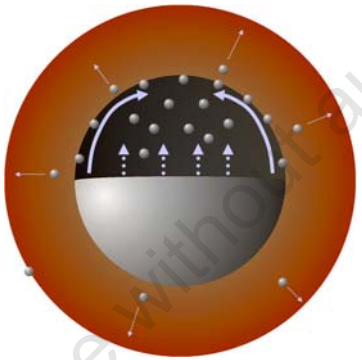
New nanocrystals for biological imaging applications



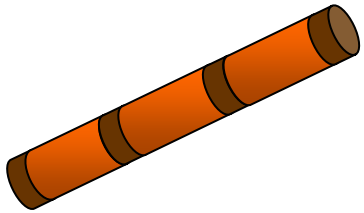
rods



tetrapods



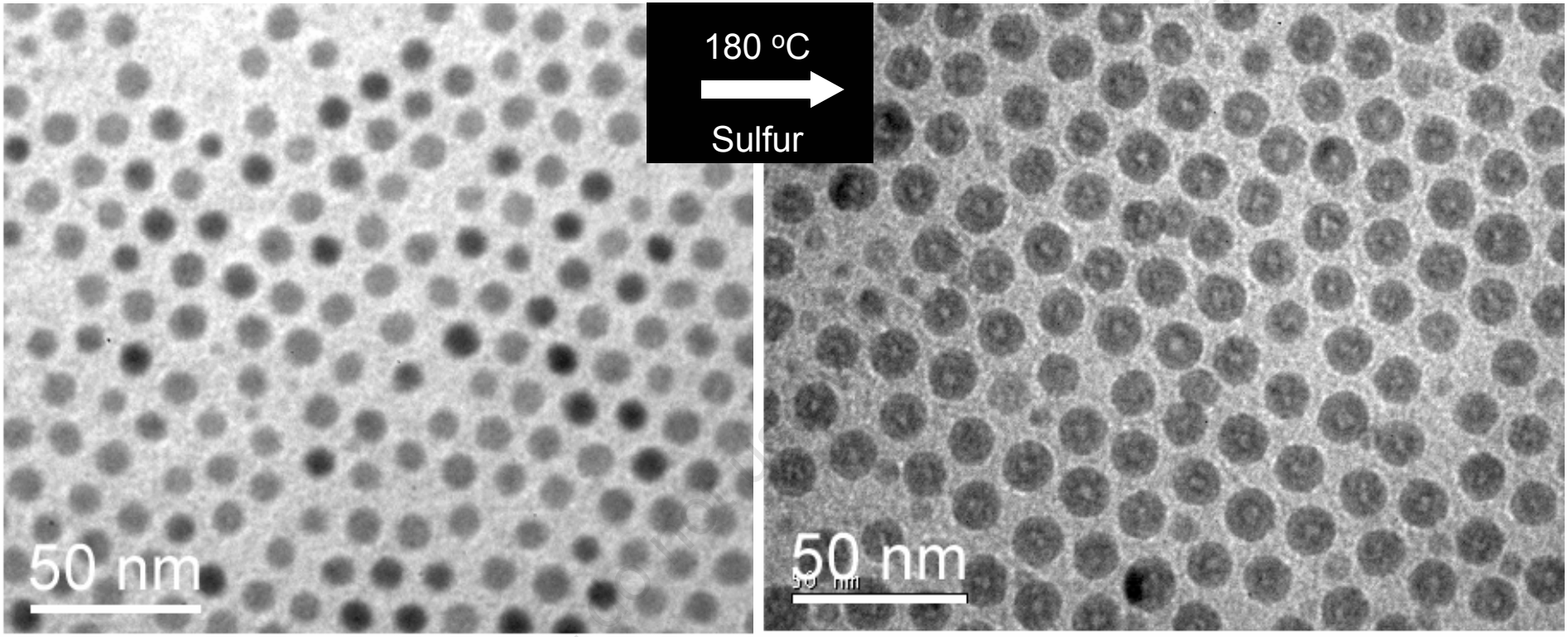
Hollow and nested



striped

Hollow nanocrystals through the Kirkendall effect

Sulfidation of Cobalt Nanocrystals



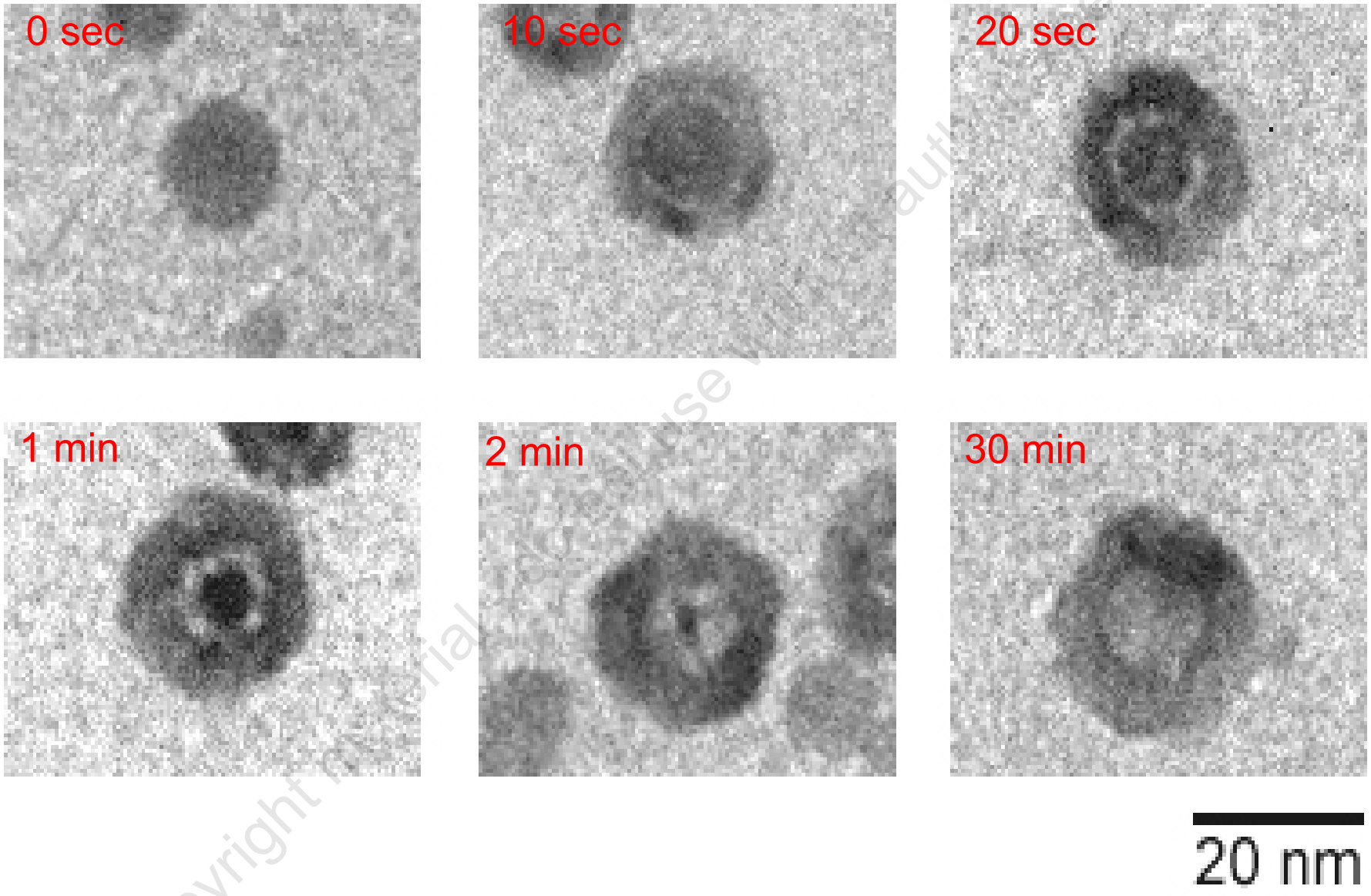
Cobalt

Hollow Cobalt Sulfide Nanocrystals

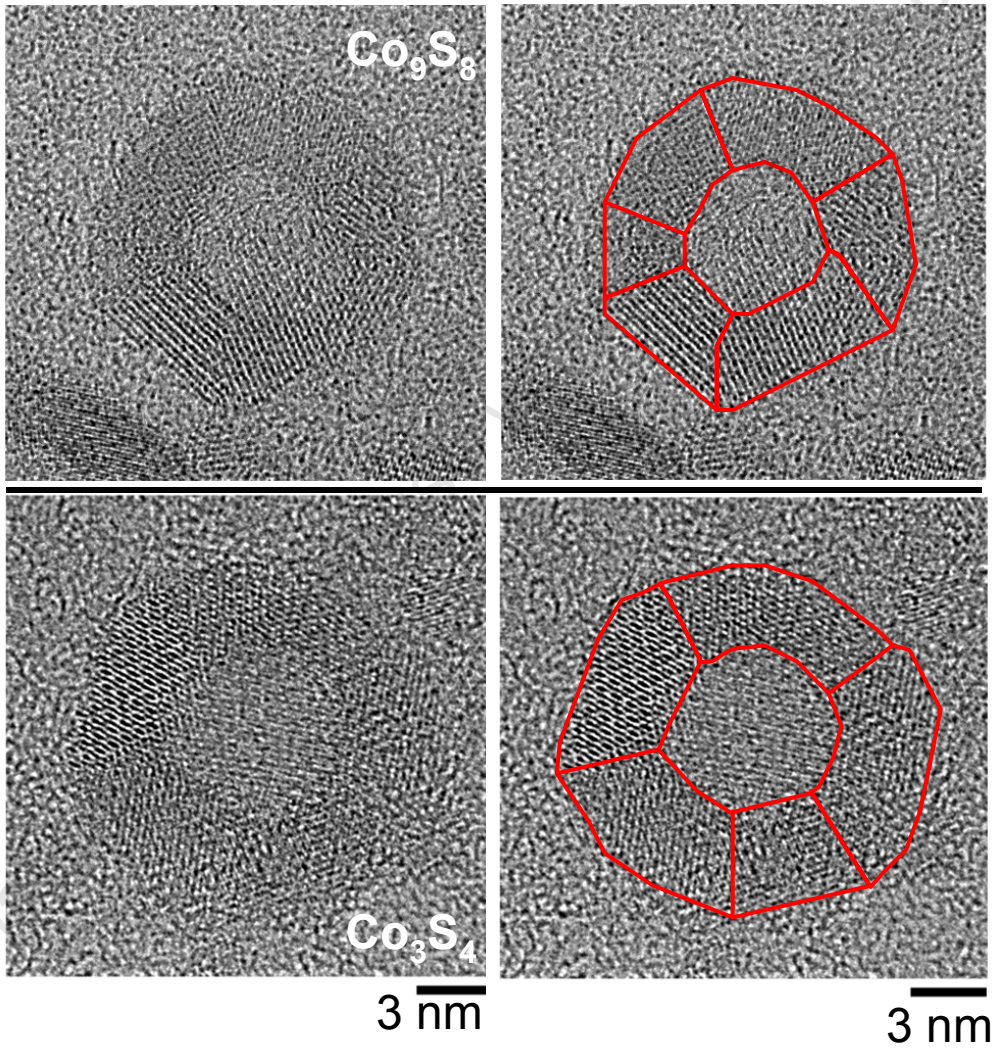
Y. Yin, R.M. Rioux, C.K. Erdonmez, S. Hughes,
G.A. Somorjai, and A.P. Alivisatos, *Science* **2004**, 304, 711

Y. Yin, C. Erdonmez, A. Cabot, S. Hughes, A. P. Alivisatos
Advanced Functional Materials 16 (11): 1389-1399 Jul 21 2006

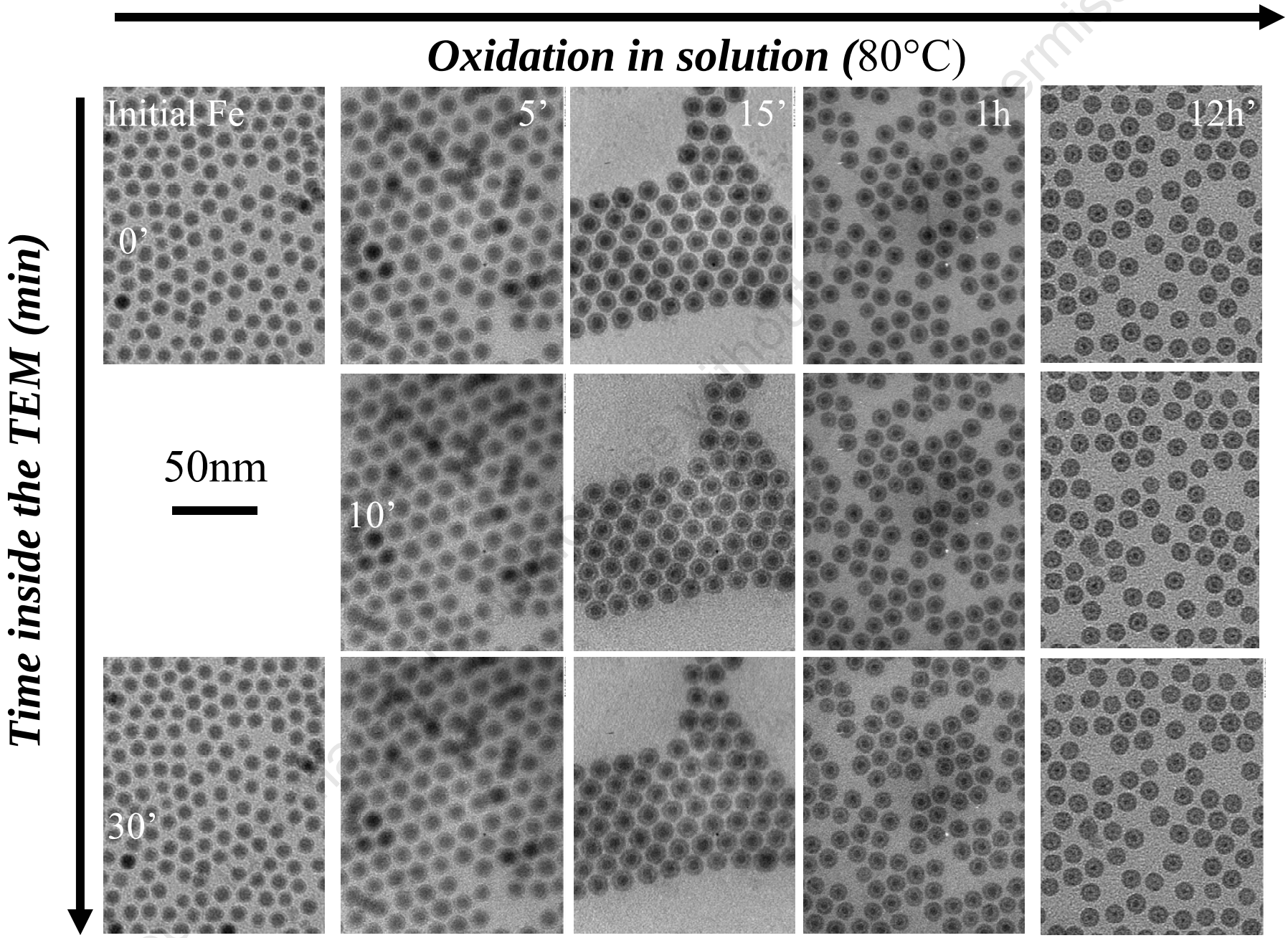
Evolution of the pore structure-- Cobalt Selenide



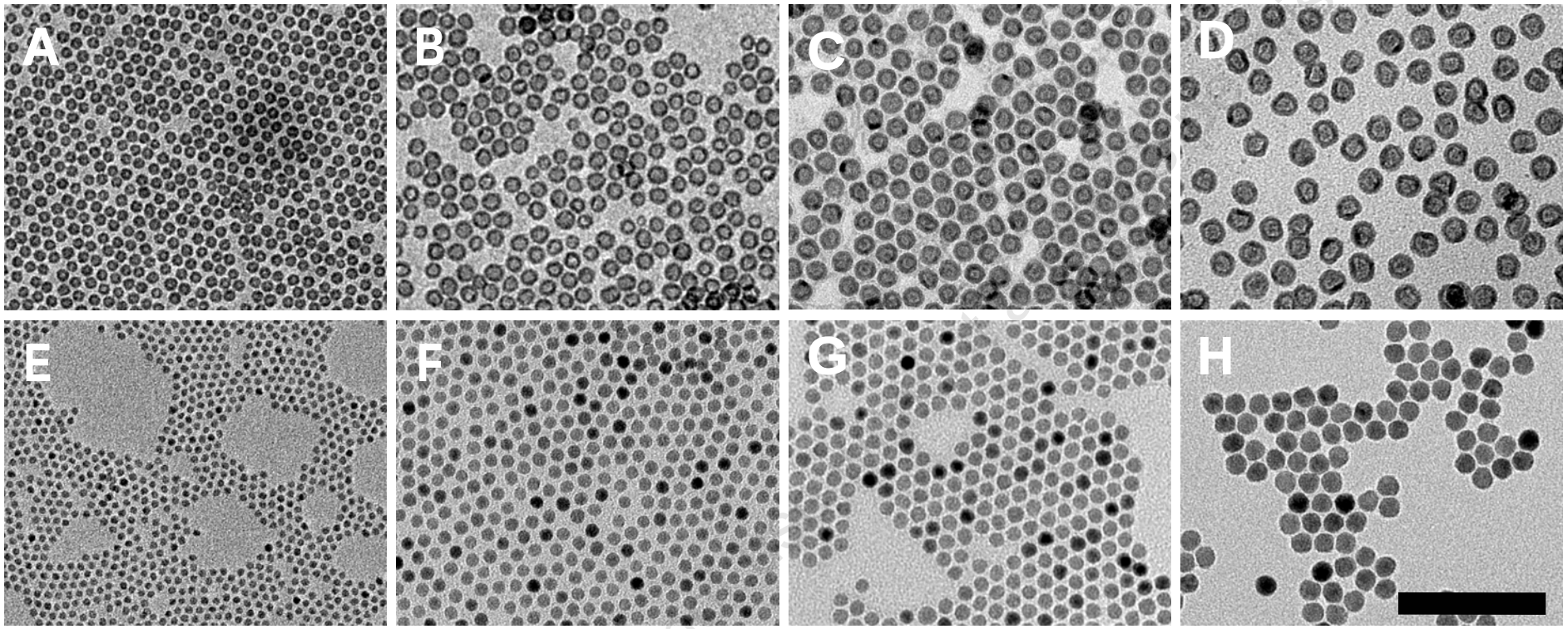
Segmented polycrystalline structure of the hollow walls

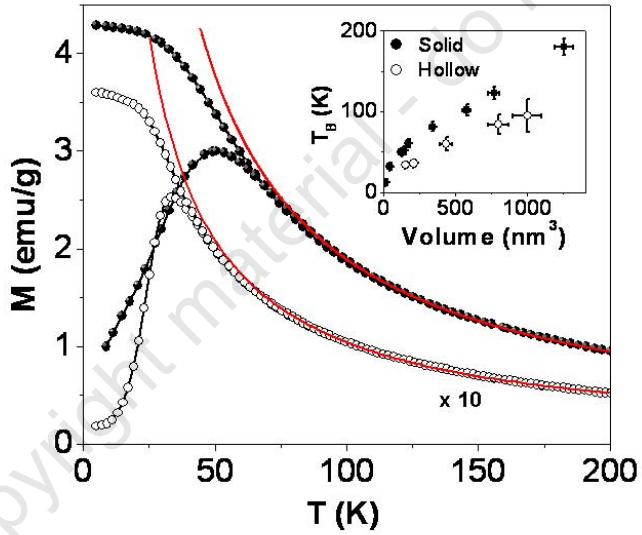


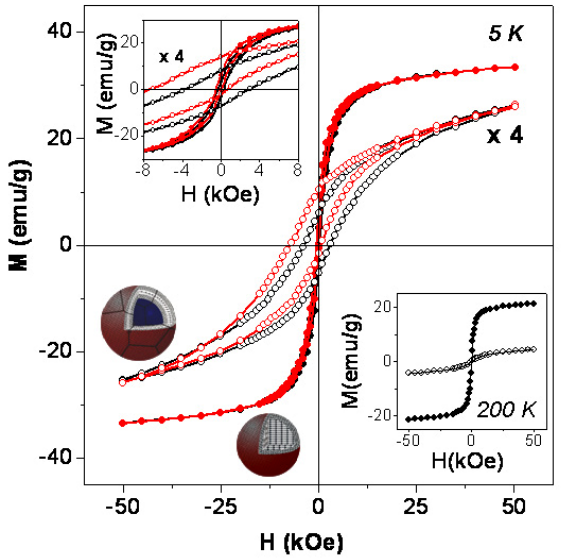
Hollow Iron Oxide formation – single central pore



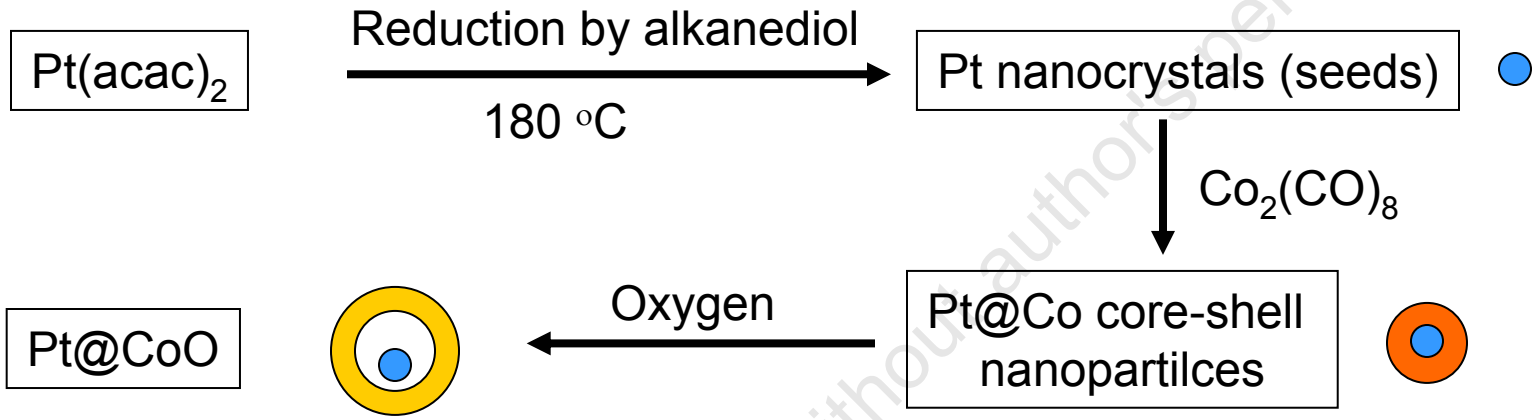
Magnetization studies of hollow vs. solid iron oxide nanoparticles

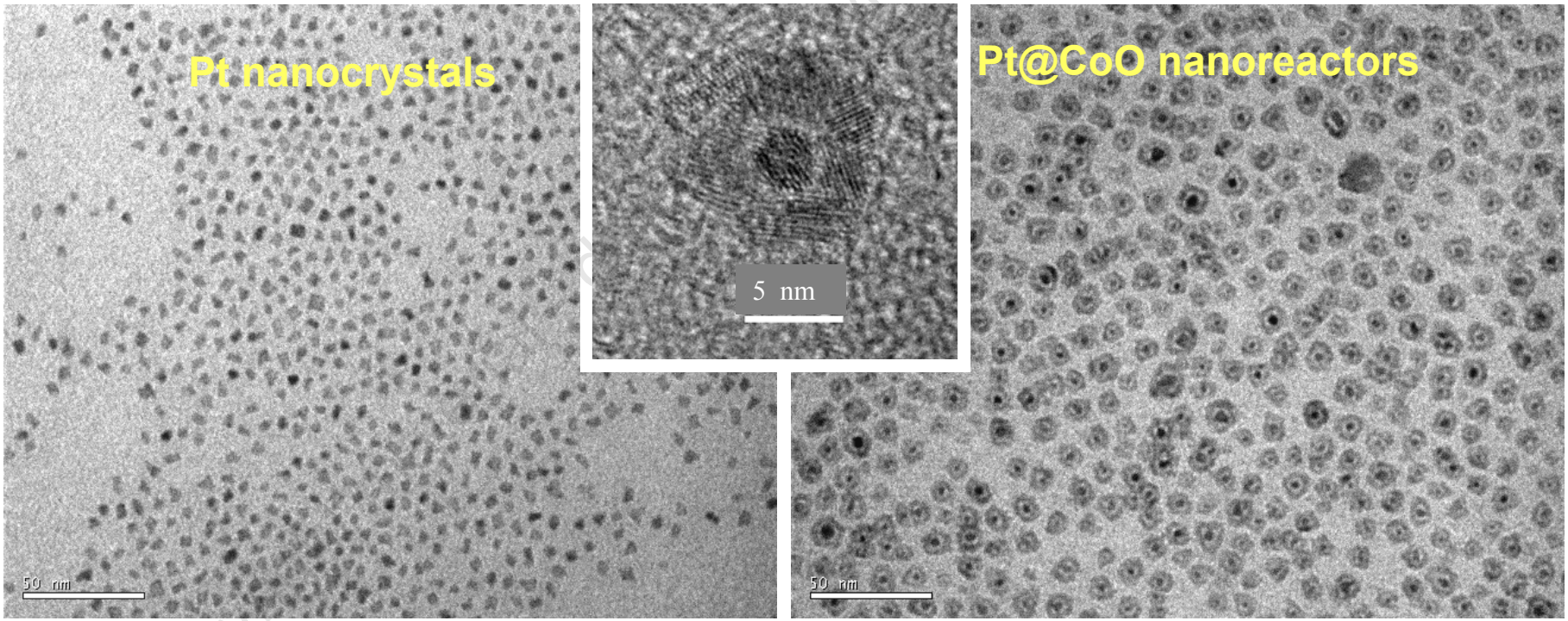




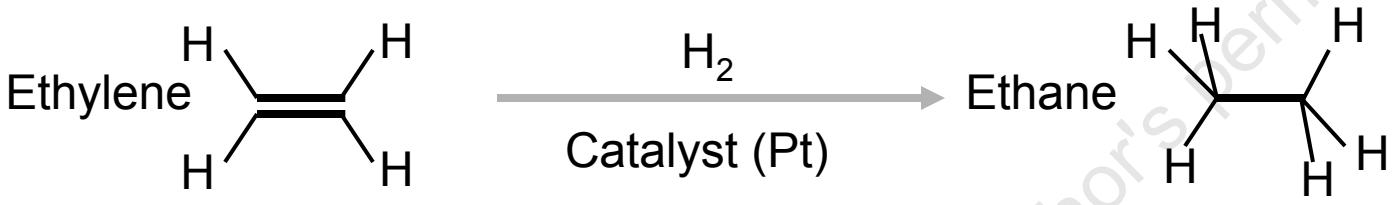


Pt@CoO nanoreactors for catalytic applications

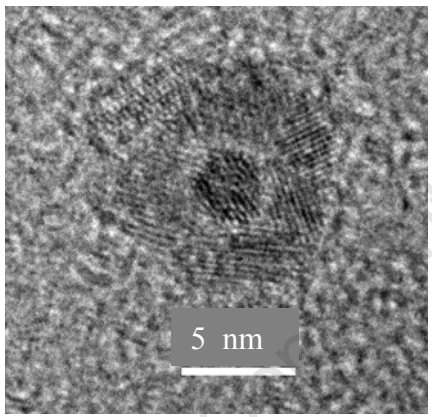




Hydrogenation Reaction of Ethylene

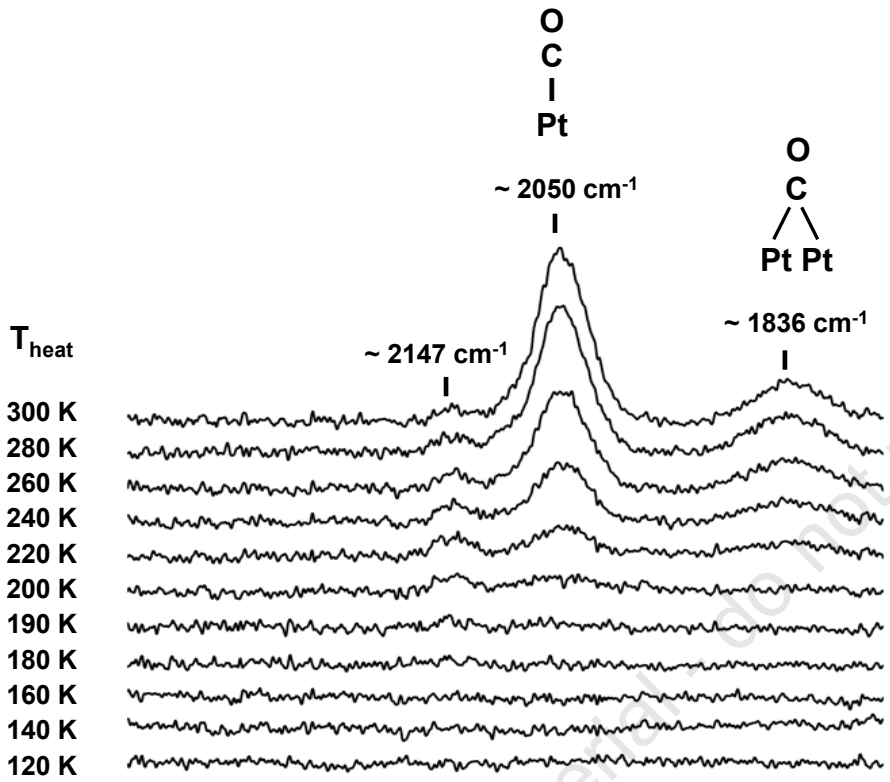


	Temperature (°C)	Pretreatment	Catalytic Activity
Pt@CoO	-45	No	**Yes**
	RT	No	Yes
	100	H_2 1hr	Yes
CoO (hollow spheres)	RT	No	No
	100	H_2 1hr	**No**
	200	H_2 1hr	Yes

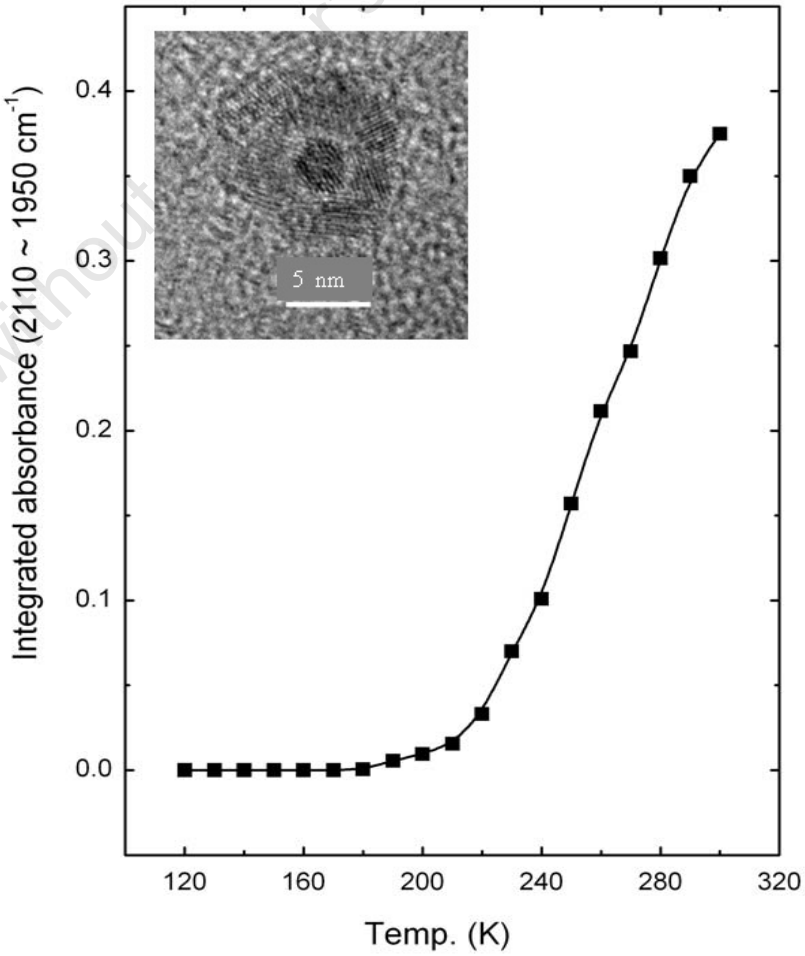


IR study of CO diffusion through shell upon heating

Difference spectra (ref. 110 K, CO 2 Torr)

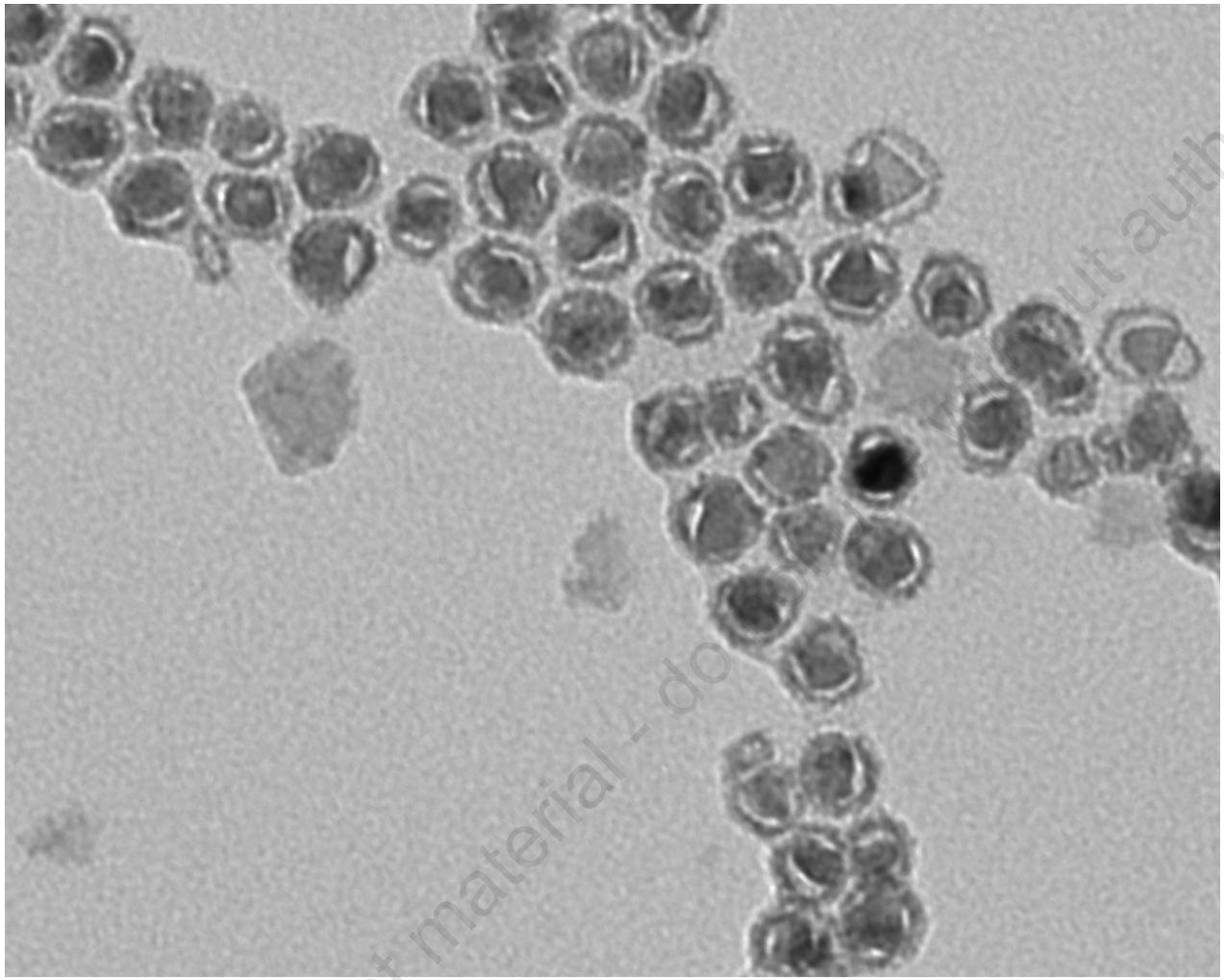


Pt@CoO



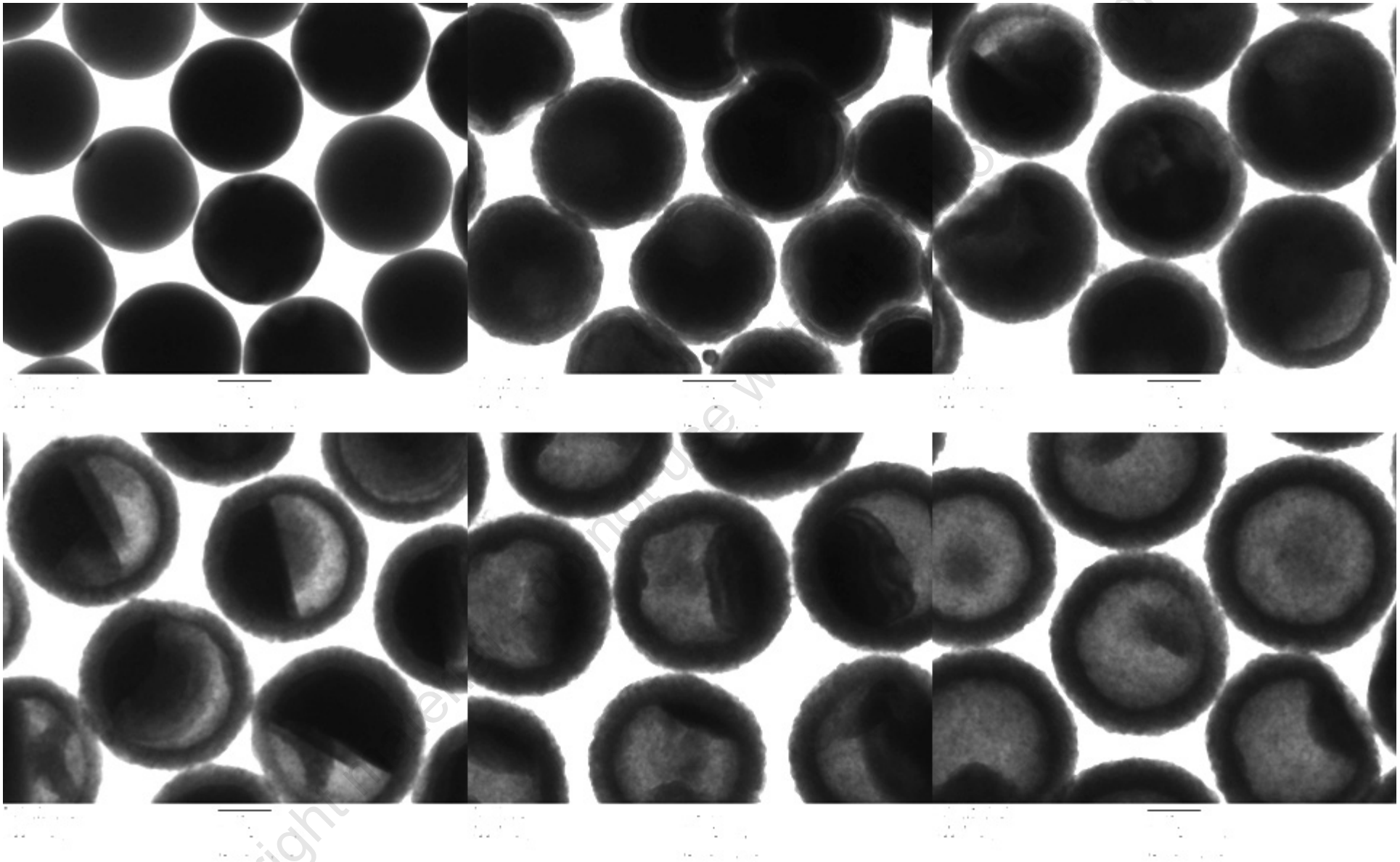
Sunhee Kim and Prof. John T. Yates, Jr

Ag nanocrystals inside Cobalt Oxide
Plasmon probing of the interstitial regions?

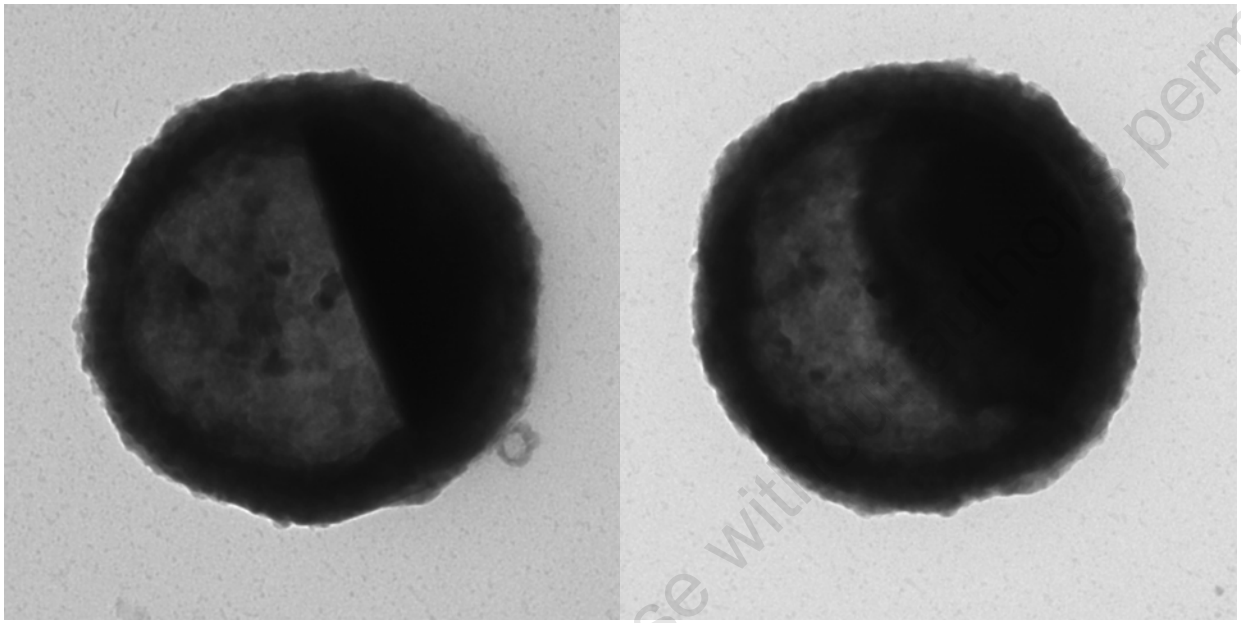


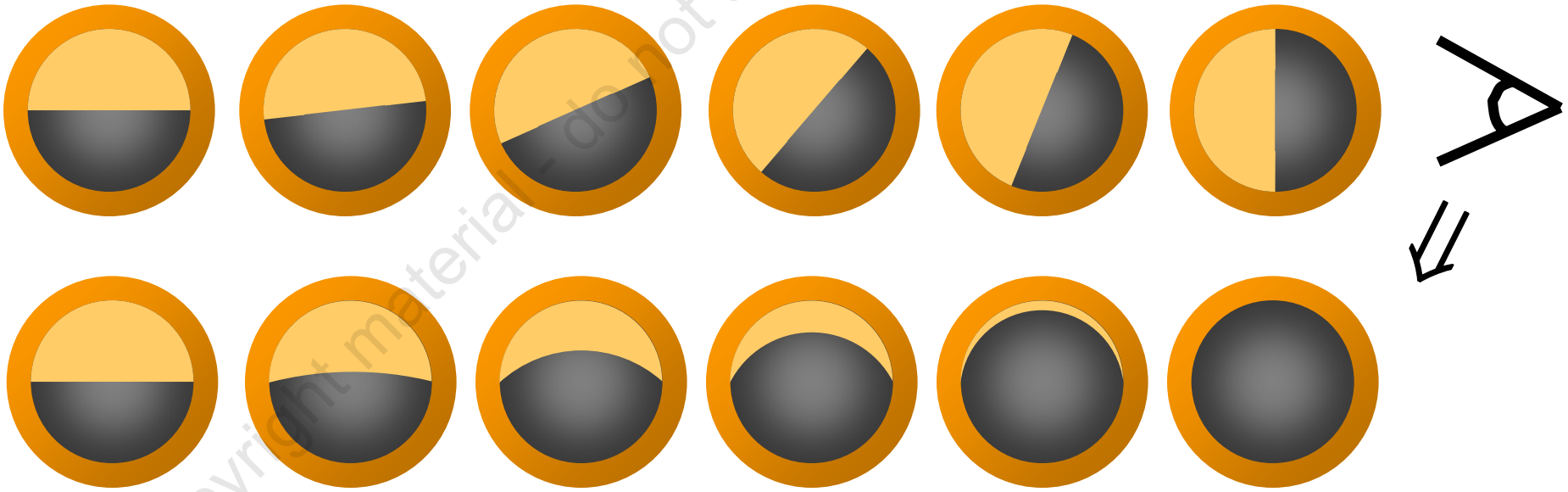
Evolution from Cd to hollow CdS

T = 220 ^{0}C



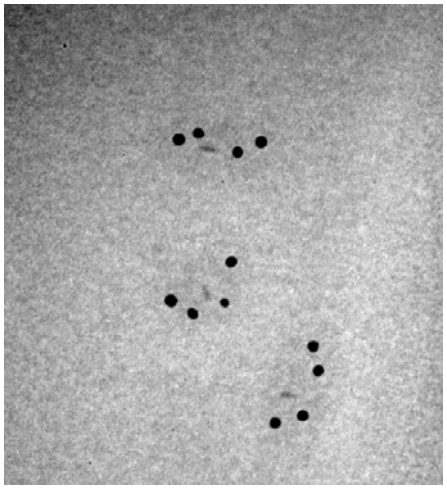
The free Cd surface is flat

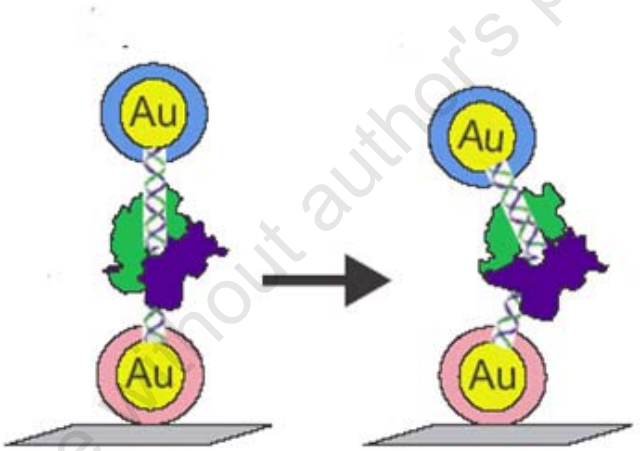




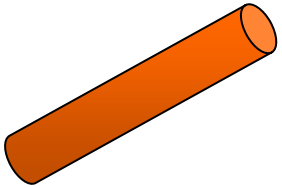
Nanocrystal Molecules and plasmon ruler study of ECO RV DNA cleavage

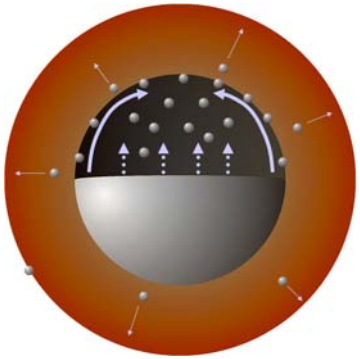
Björn Reinhardt, Sassan Sheikolislami,
(Carsten Sönneschsen), Prof. Jan Liphardt

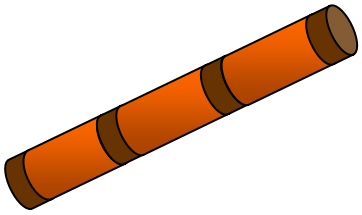




New nanocrystals for biological imaging applications







Paul Alivisatos
Lawrence Berkeley National Lab and University of California, Berkeley