SAND2006-7352C

Synthesis and Light-induced Assembly of Photo-responsive Colloids

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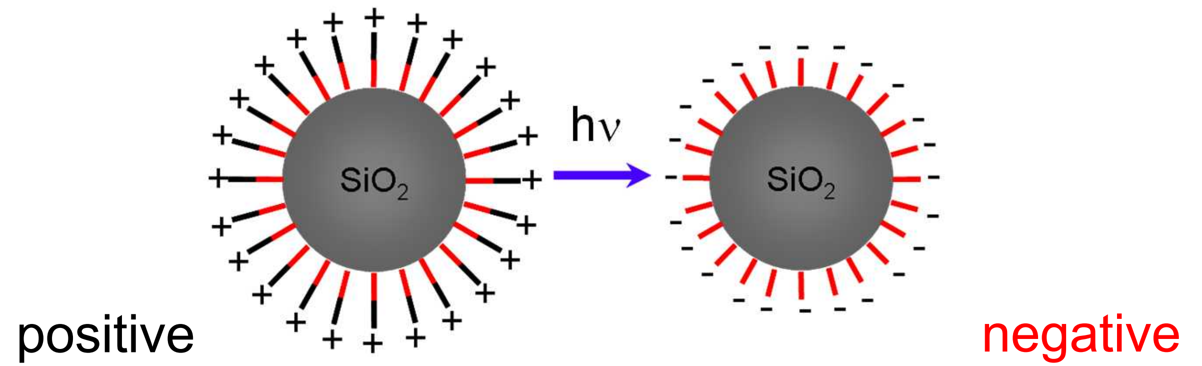
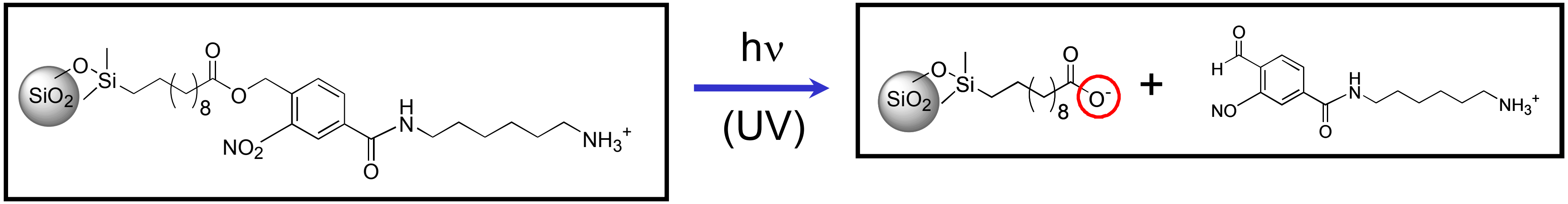
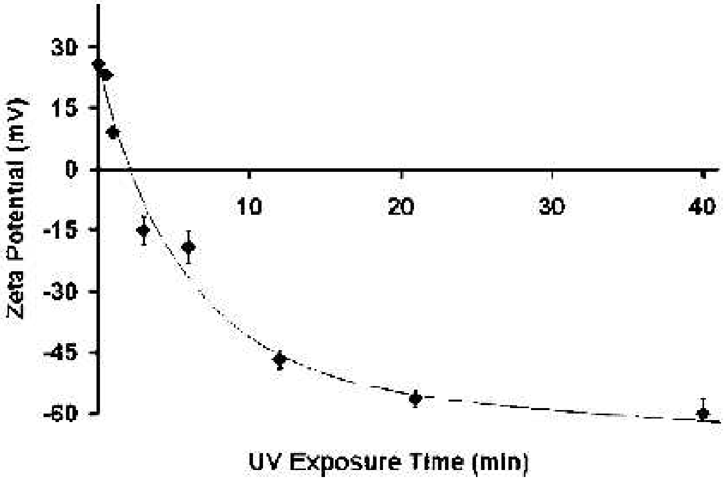
2. Chemistry, University of Illinois, Urbana, Illinois
3. Electronic and Nanostructured Materials, Sandia National Laboratories, Albuquerque, New Mexico.

Light-regulated colloidal surface charge





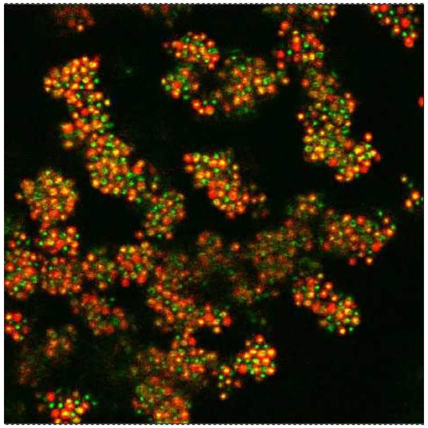
Particle zeta potential control (at neutral pH) via UV irradiation.



K.N. Plunkett, A. Mohraz, J.A. Lewis, and J.S. Moore, *J. Am. Chem. Soc.* **127**, 14574 (2005)

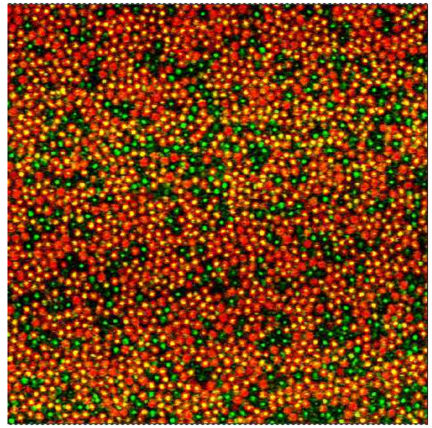
Light-regulated interactions in binary suspensions

colloidal gel



$\xrightarrow{h\nu}$

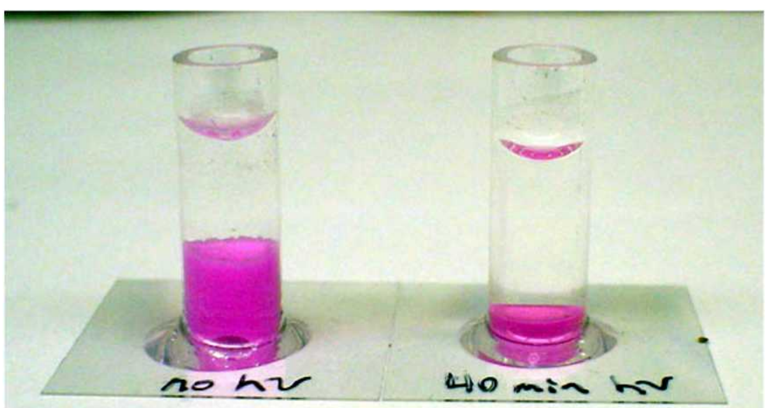
stable colloidal fluid (sedimented)



Mixture of negatively-charged (shown as orange) and surface-modified (shown as green) particles

Colloid	surface charge	
	Initial	Post UV
bare silica	-	-
SM silica	+	-

colloidal sediments



Other architectures:

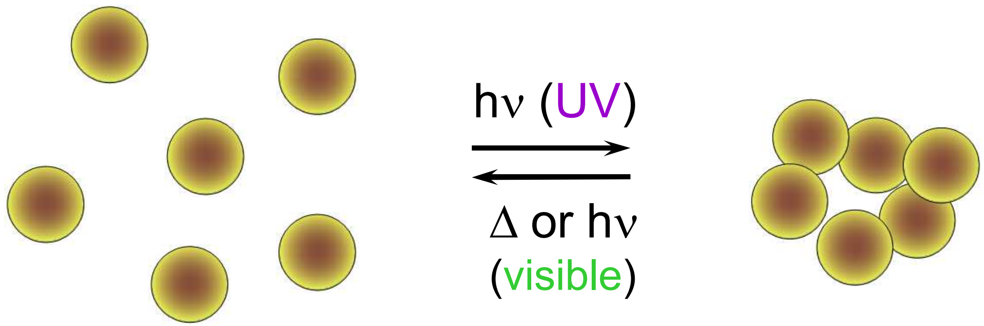
$(-) \xrightarrow{h\nu} (+)$

hydrophobic $\xrightarrow{h\nu}$ $(-)$

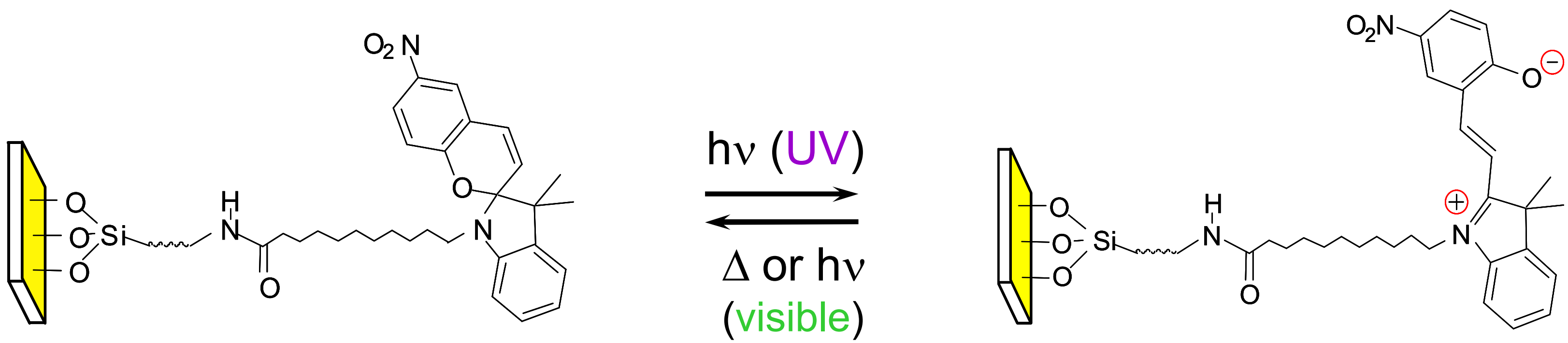
hydrophobic $\xrightarrow{h\nu}$ $(+)$

K.N. Plunkett, A. Mohraz, J.A. Lewis, and J.S. Moore, *J. Am. Chem. Soc.* **127**, 14574 (2005)

Reversible light-regulated colloidal interactions??



Approach: Utilize reversible photochemical reaction



closed form

Spirobenzopyran (SP)

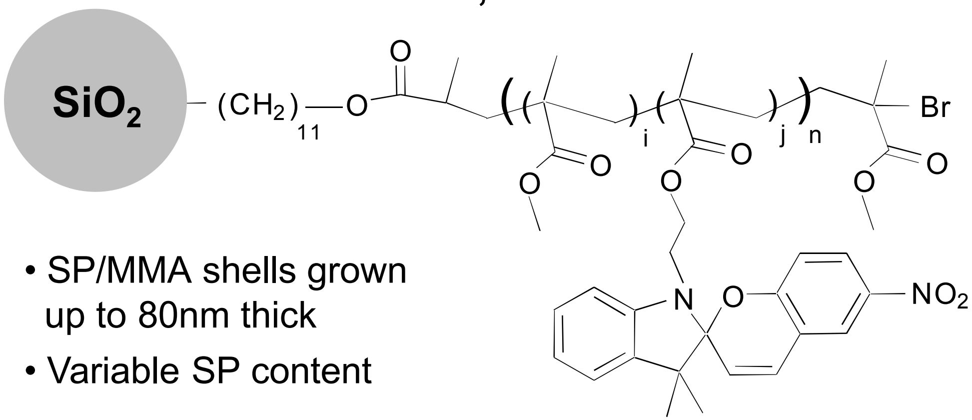
zwitterionic form

Merocyanine (ME)

- Reversible aggregation of SP-coated colloidal particles in non-polar solvents
  K. Ichimura, et al. *J. Mat. Chem.* **4**, 883 (1994)

Photo-reversible copolymer brush layer

Silica core, SP-co-MMA shell



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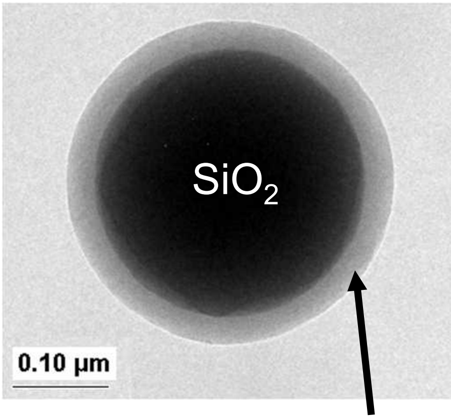


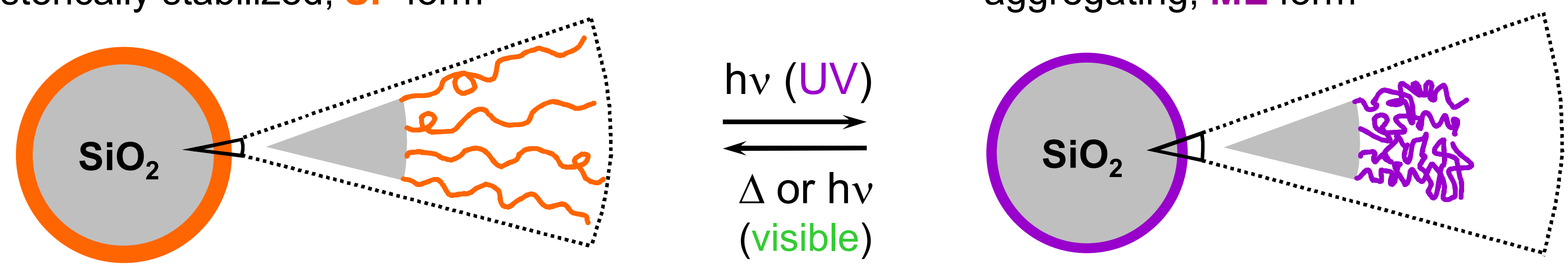
polymer brush layer

- SP/MMA shells grown up to 80nm thick
- Variable SP content

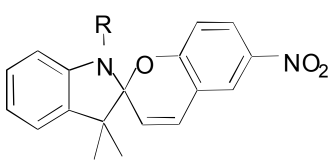
M. Piech, N.S. Bell, *Macromolecules* **39**, 915 (2006)

sterically stabilized, **SP** form

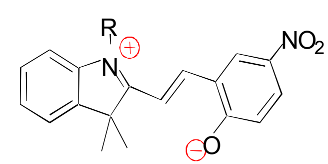
aggregating, **ME** form



SP = closed form

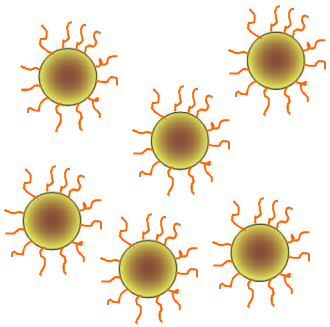


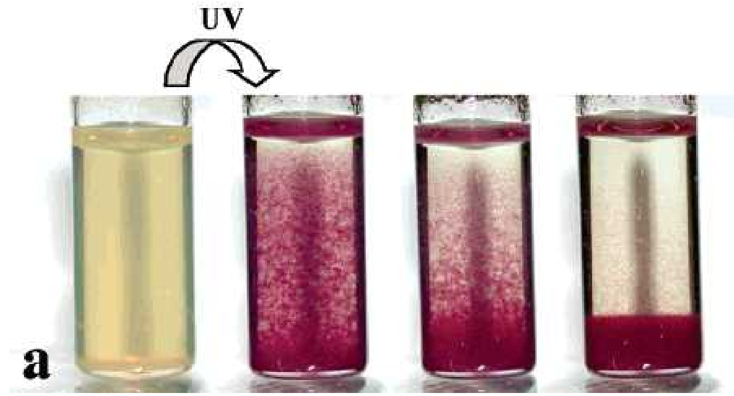
ME = zwitterionic form

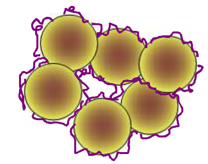


N. S. Bell, M. Piech, *Langmuir*, ***22*** *(2006)* 1420-1427

Conformation behavior under stimuli

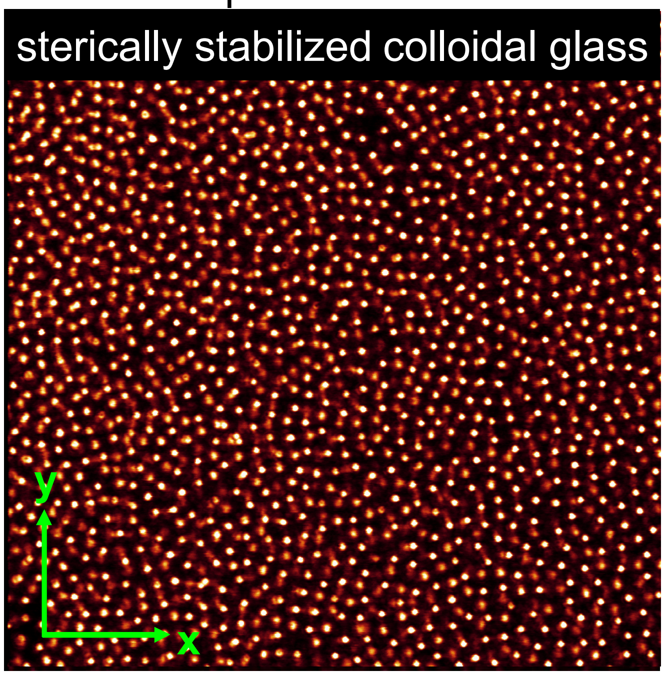






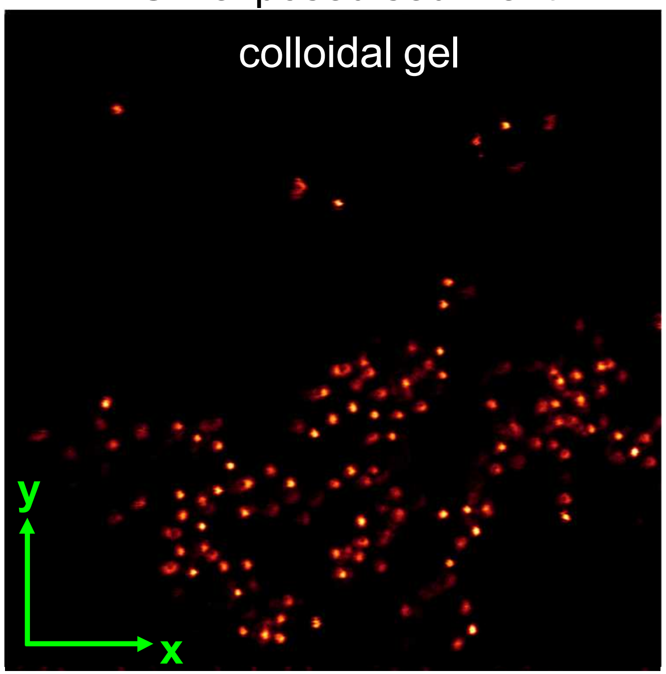
N. S. Bell, M. Piech, *Langmuir*, ***22*** *(2006)* 1420-1427

unexposed sediment

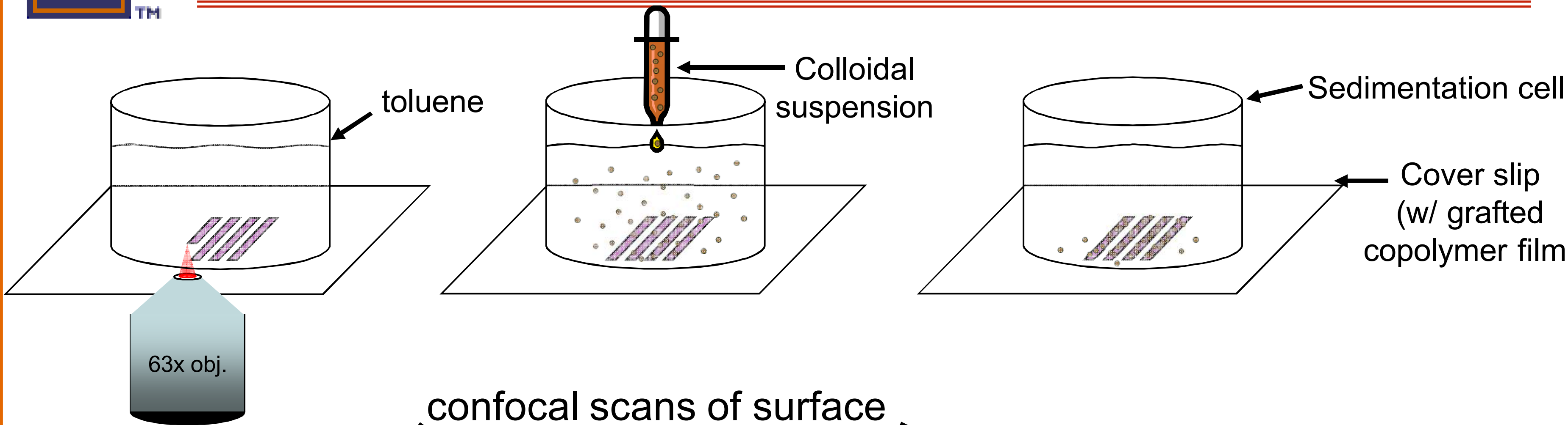


$$\underset{\Delta \text{ or Vis.}}{\overset{\text{UV}}{\rightleftharpoons}}$$

UV exposed sediment

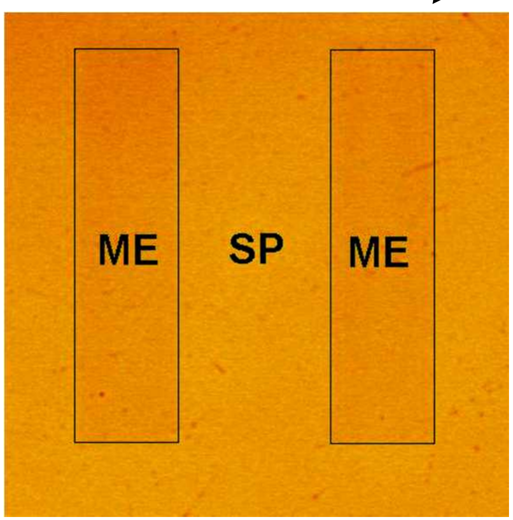


2D photo-defined colloidal adsorption

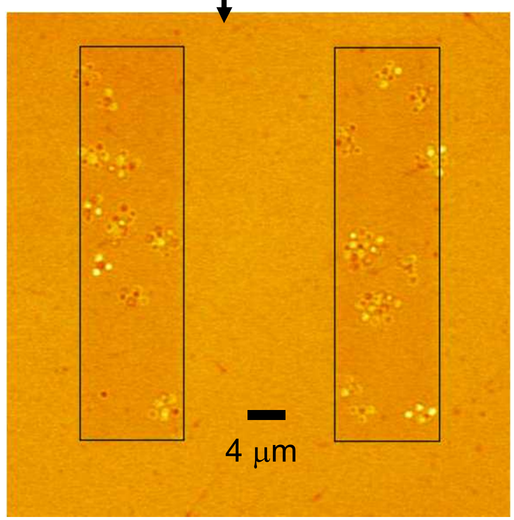


confocal scans of surface

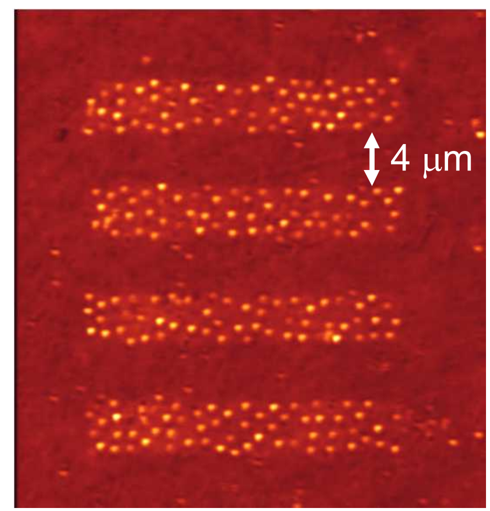
2D patterning example



exp. start, t = 0



clusters, t = 660 s



M. Piech, M. C. George, N. S. Bell and P. V. Braun:, *Langmuir*, **22**, 1379-1382 (2006)

3D laser gel-writing in colloidal sediments

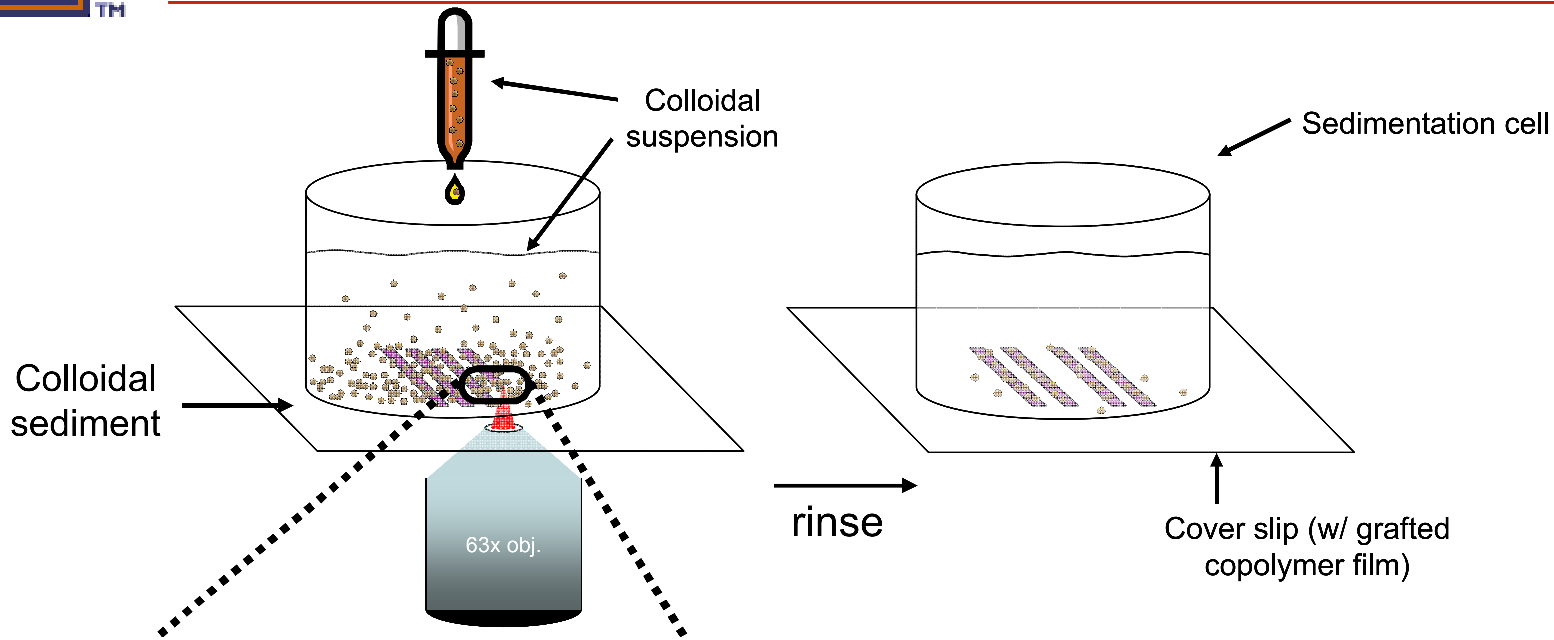
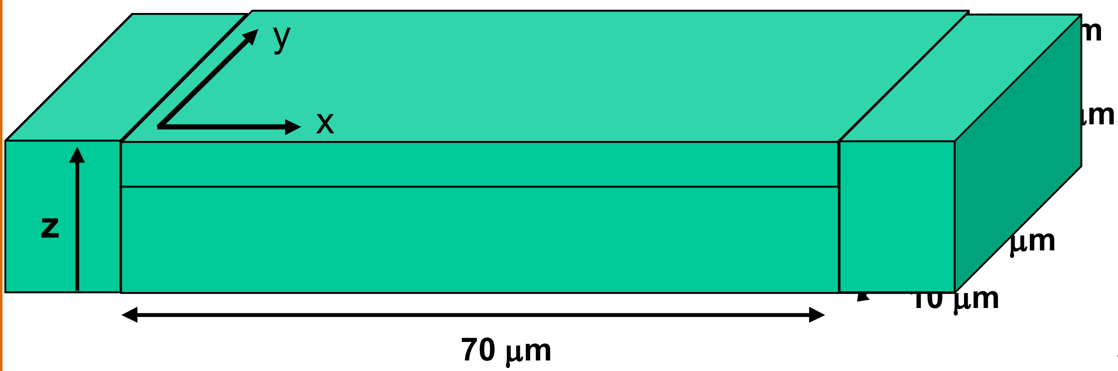
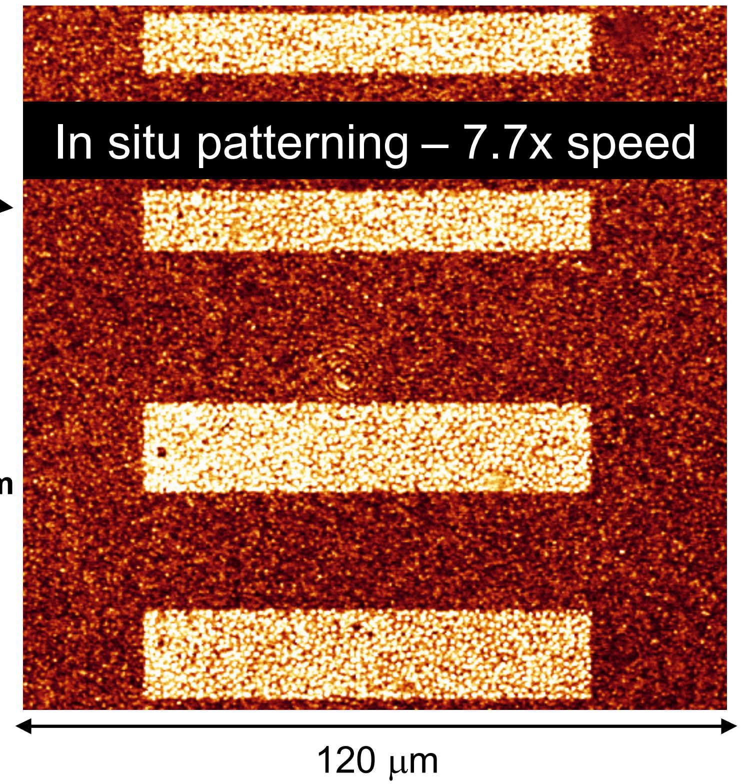


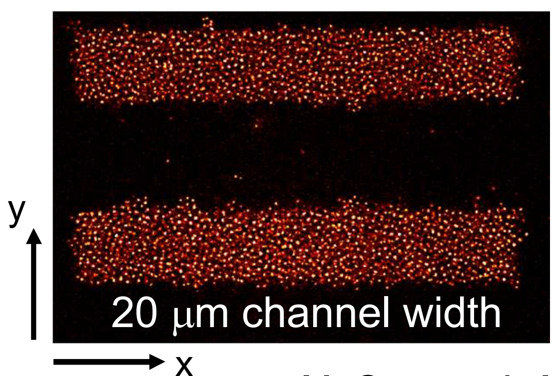
Photo-patterned colloidal gel micro-channels

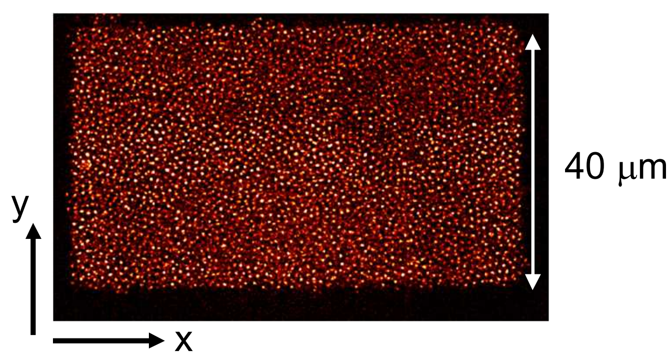
Processing Steps

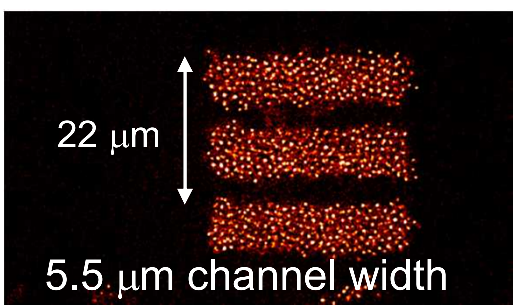
- Introduce colloids, form sediment
- Write walls (via 2PA)
- Write channel top
- Rinse out un-gelled colloids







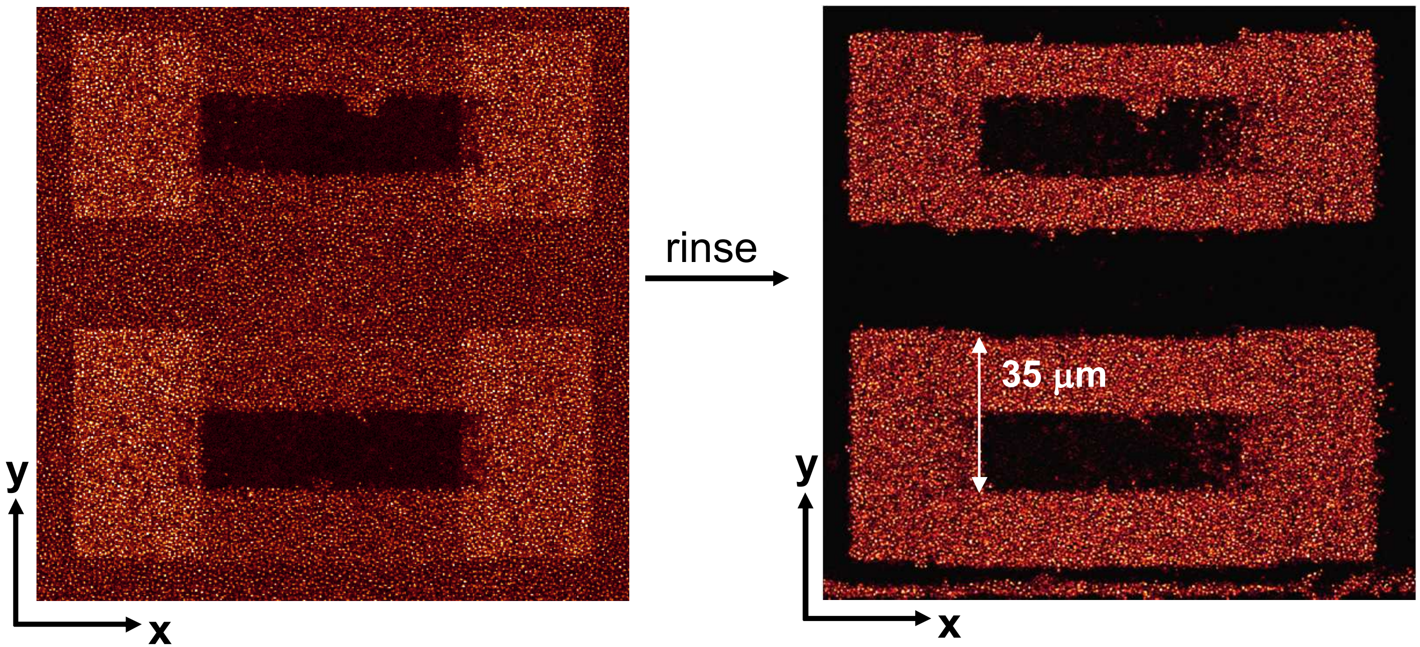




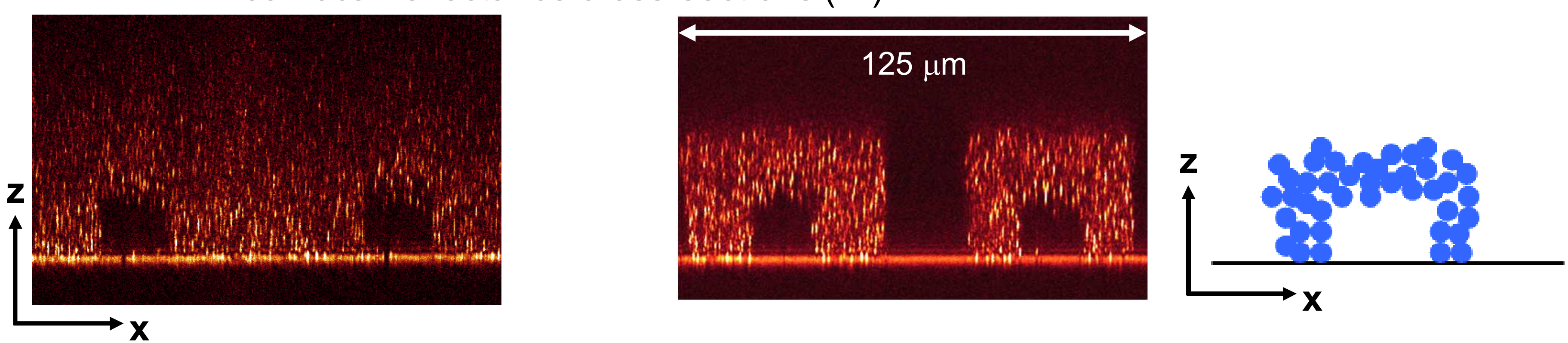
M. George, A. Mohraz, M. Piech, N. Bell, J. Lewis, and P. Braun (unpublished work)

Photo-patterned colloidal gel 3D micro-cavity

confocal xy reflectance sections

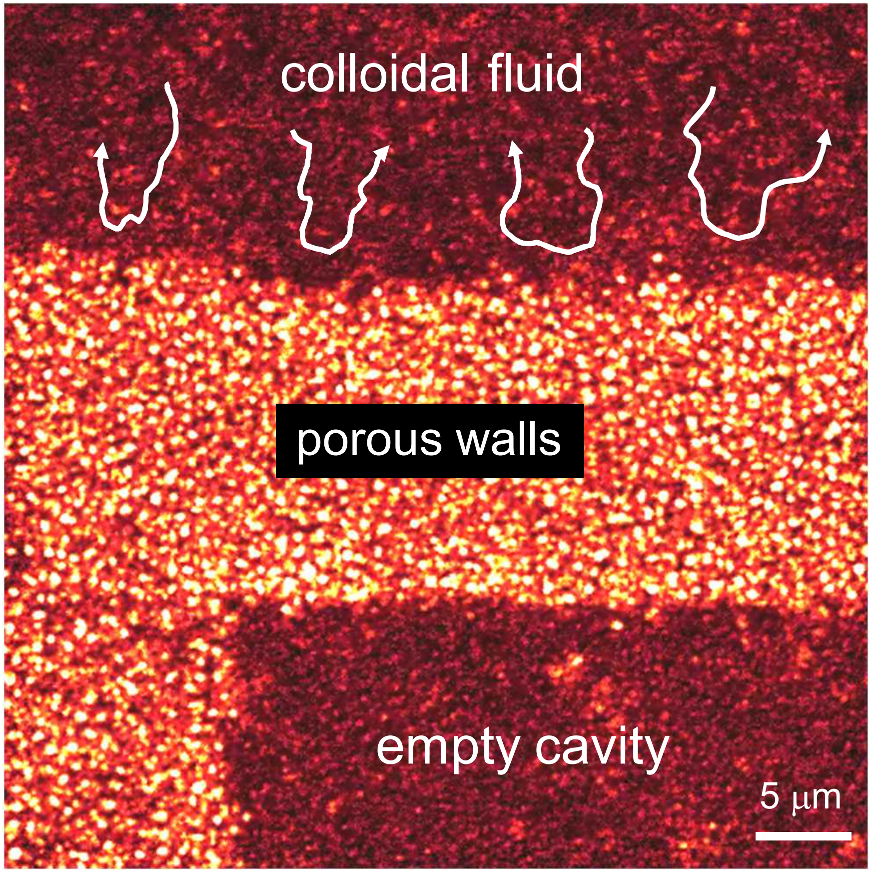


confocal reflectance cross-sections (xz)



Semi-permeable colloidal gel walls

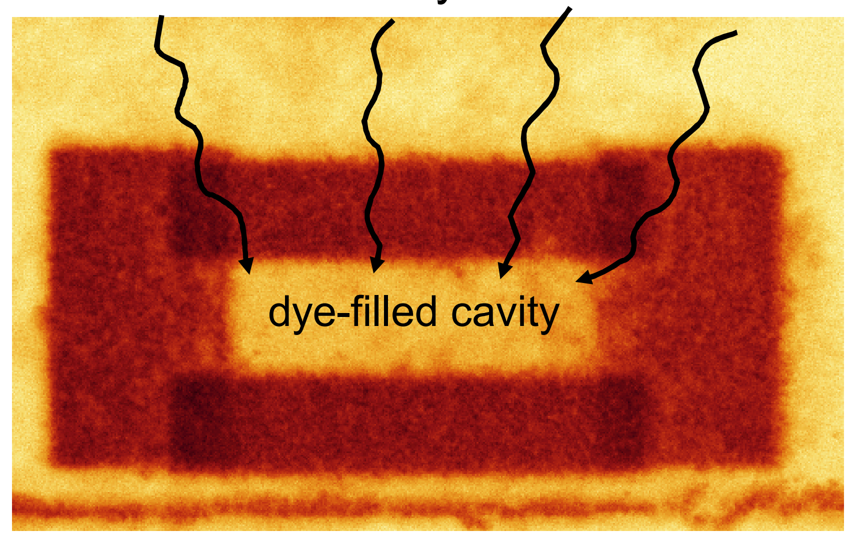
colloidal particle repulsion



confocal reflectance xyt series

7.7x speed

fluorescent dye infiltration



confocal fluorescence xy section

colloidal gel walls:

- exclude 450 nm colloids
- permeable to fluorescent dye

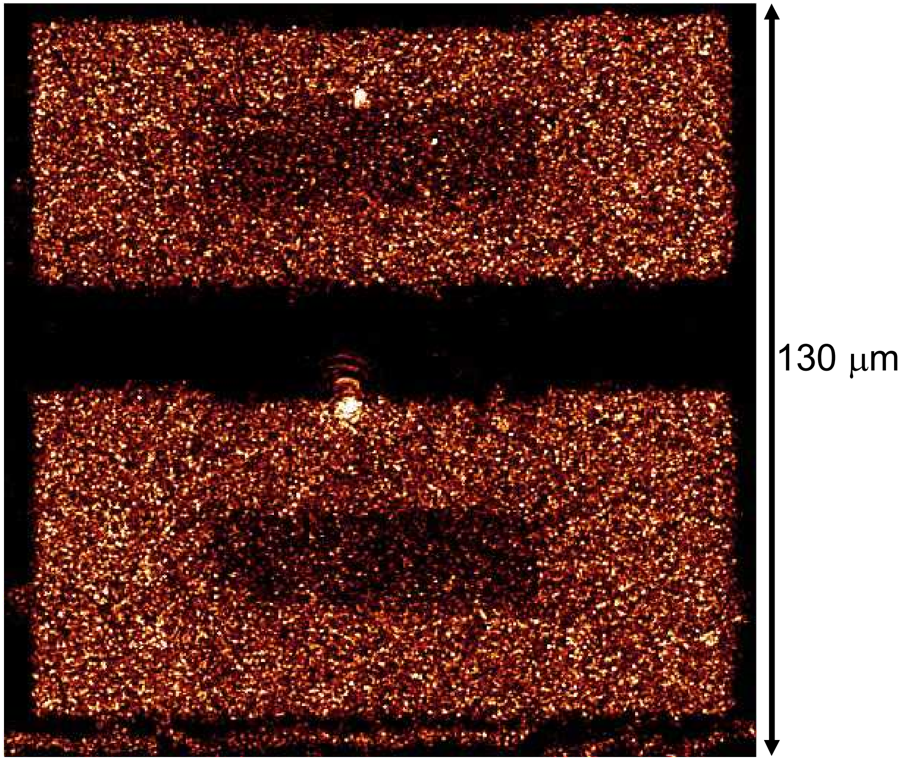
M. George, A. Mohraz, M. Piech, N. Bell, J. Lewis, and P. Braun (unpublished work)

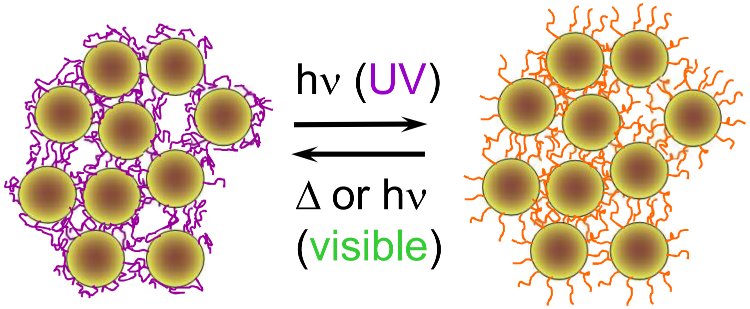
Photo-responsive colloidal system

3D laser gel writing

Applications

- Trapped colloidal fluid
  - Study of confined colloidal fluids
  - Catalytic regeneration in microfluidic reactors
- Colloidal Ink based 3D photolithography
- Nanofiltration with dynamic remote control of pore size





Reversible size selective photo-gating??

Acknowledgments

Additional contributors:

- Jacinta Conrad
- Stephanie Pruzinsky

Facilities:

- Sandia National Laboratory; Albuquerque, NM
- Beckman Institute Microscopy Suite; Urbana, IL
- Frederick Seitz Materials Research Laboratory; Urbana, IL

Funding:

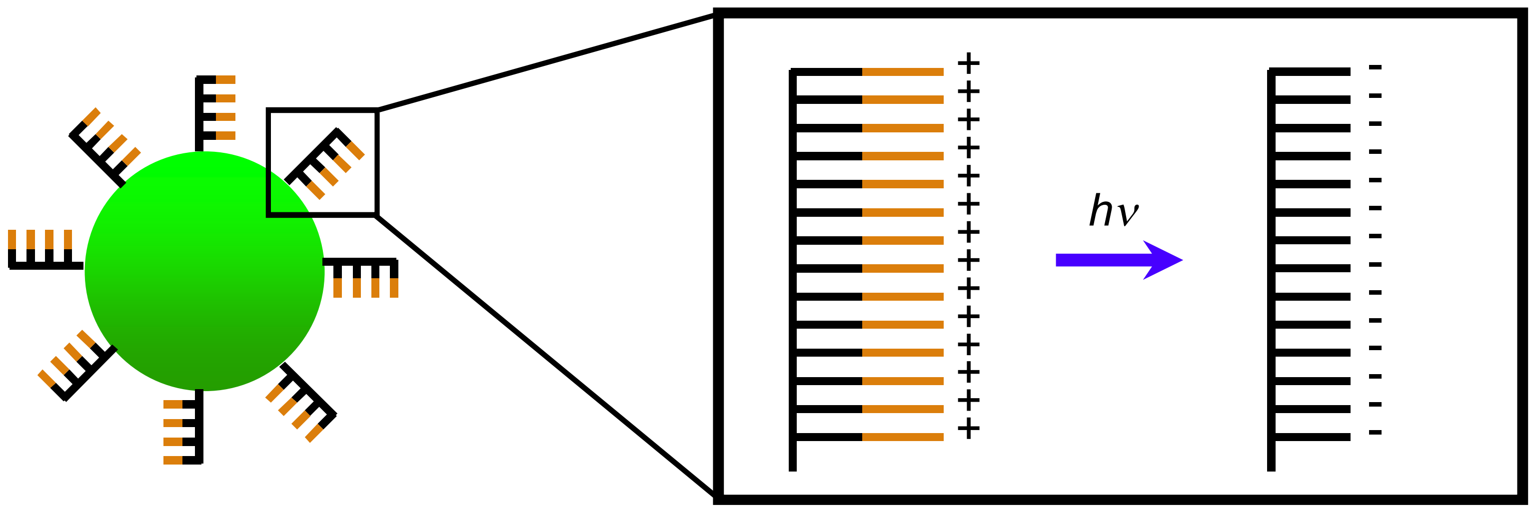
- CINT – Sandia National Laboratory
- Army Research Office – MURI Grant
- Department of Energy

Extras

MURI insignia images

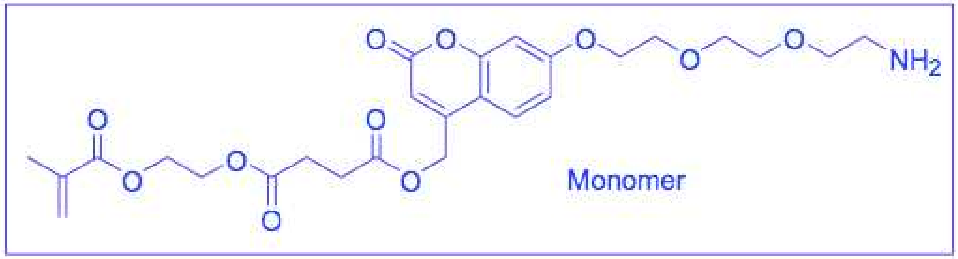
Improved photocleavable system

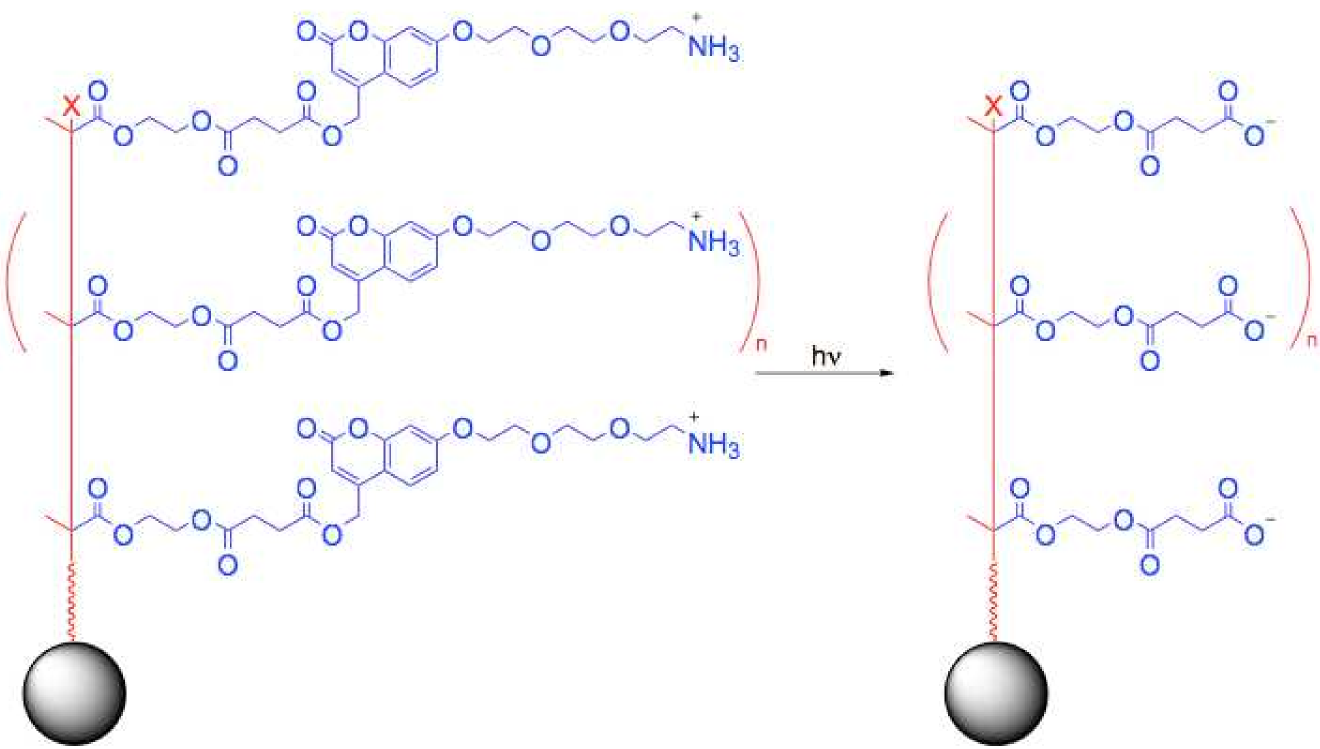
- Desired features for a photocleavable system
  - *Fast photocleavage*: charge reversal in a few seconds
  - *pH-insensitive*: cleavable over a relatively wide pH range
- Design a new photoresponsive system
  - *Photocleavable linker*: coumarin
  - *Attachment*: polymer backbone and “brush”



Collaboration with Moore group, UIUC Chemistry

Coumarin photochemistry

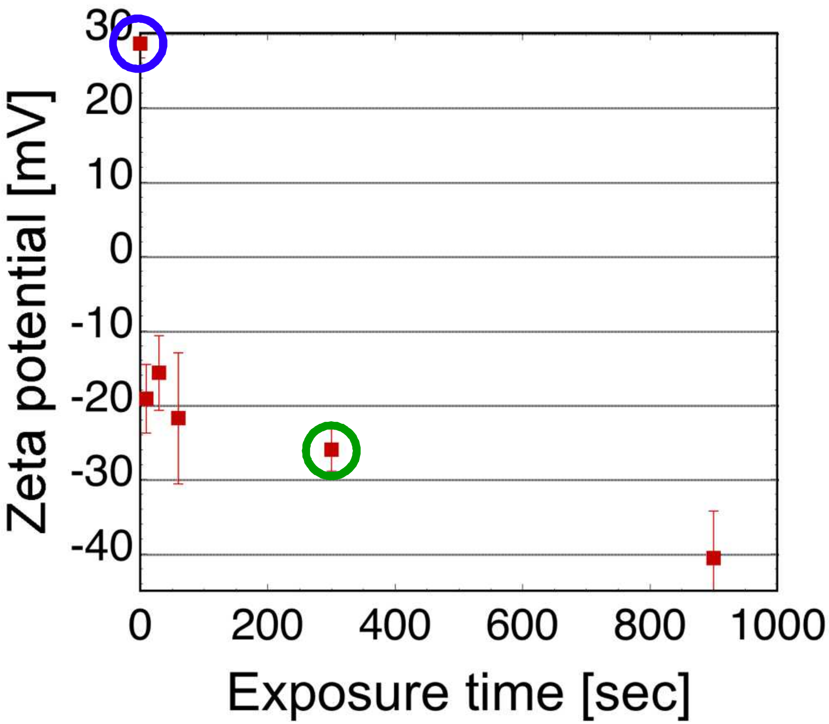


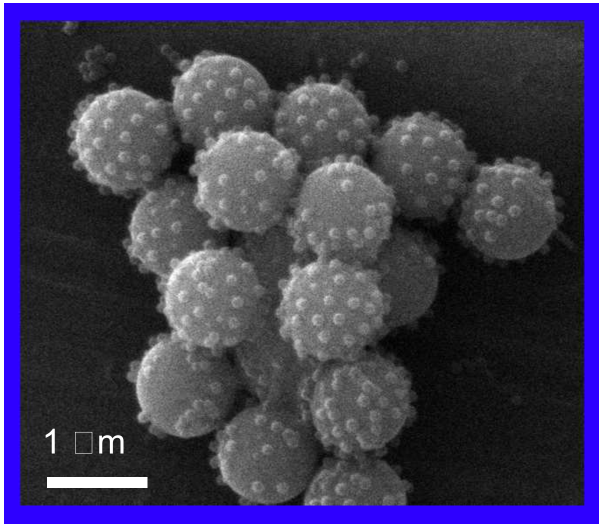


Polymer pre-exposure

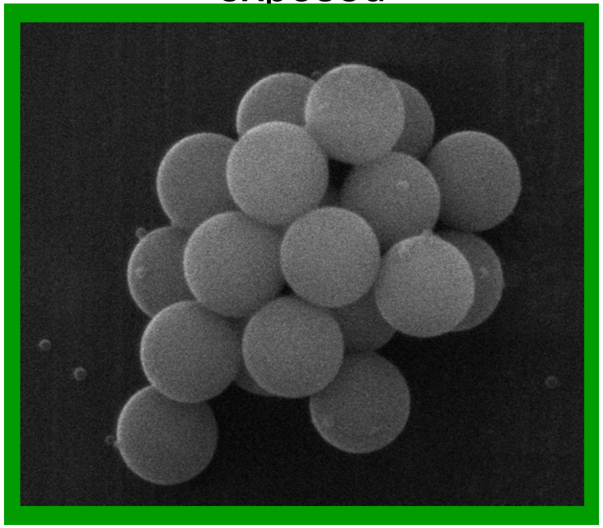
Post-exposure

Early results on coumarin system show fast cleavage





Non-exposed



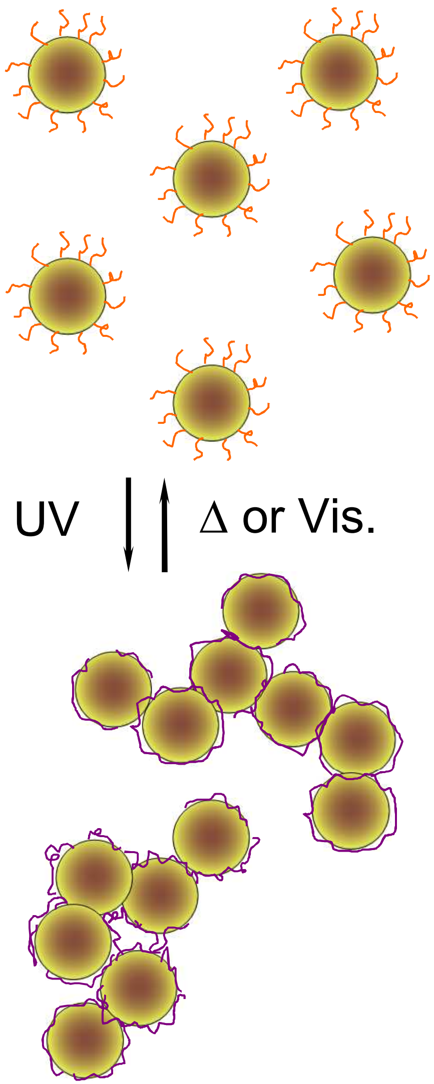
Exposed for 5 minutes

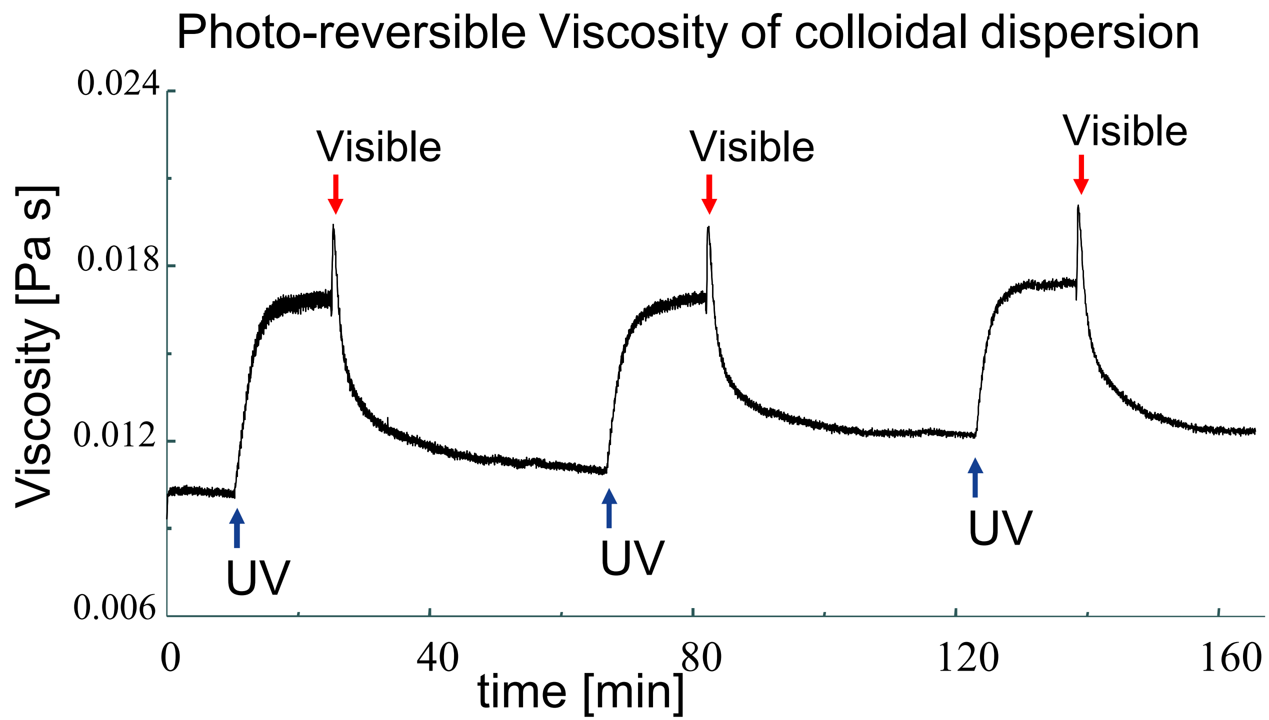
To further test, add sulfate-modified PS nanoparticles (100 nm diameter) to suspensions of coumarin-modified colloids

Photocleavable (Coumarin-based) Collaborators

- Lewis group: Ketan Bhatt
- Moore group: Nate Bowling, Josh Ritchey, and Neil Viernes

Photo-control of viscosity in colloidal systems





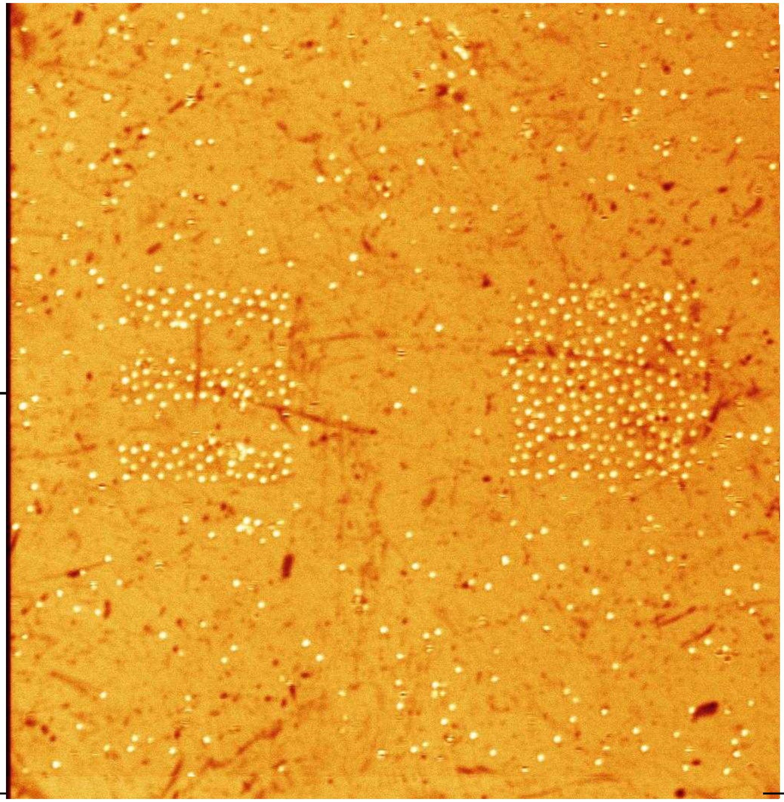
1 μm SP/MMA modified colloids in toluene at ~30 vol.%

Photo-control of colloidal interactions, CINT Workshop Poster, Martin Piech and Nelson S. Bell (Sandia National Laboratories, NM), Paul Braun and Matthew George (University of Illinois at Urbana-Champaign)

Multiphoton patterning to control colloid adsorption

images taken in flow cell with toluene as solvent

Photo-switched (open form)

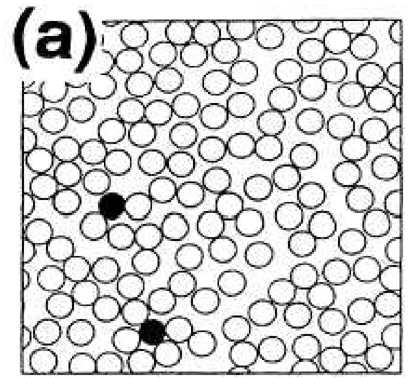


Poly SP/MMA (closed form) end-grafted onto fused silica substrate

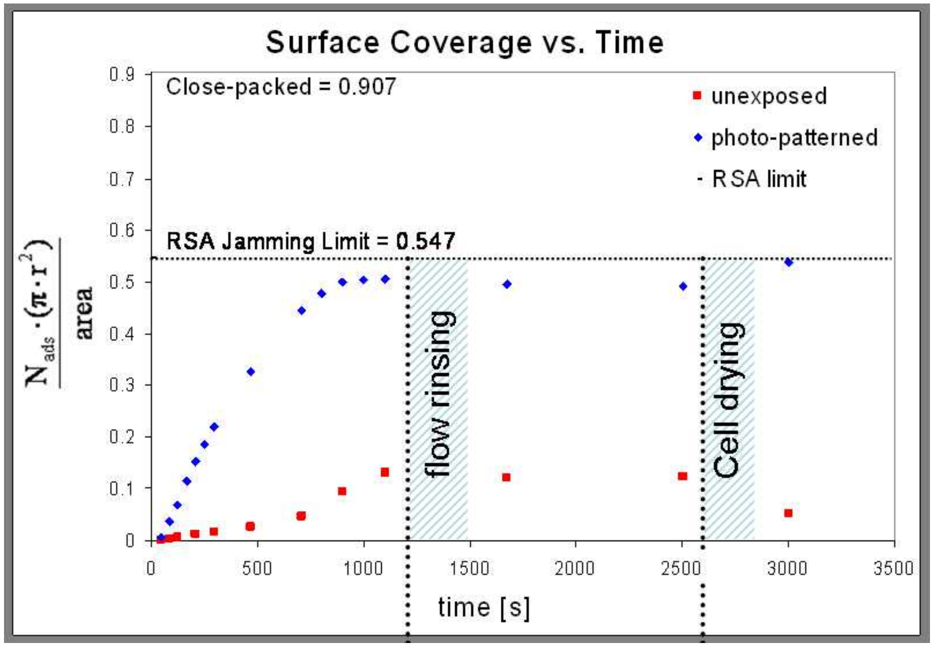
After colloid addition, settling, rinse

Adsorption kinetics

RSA of Disks $\Rightarrow$ Jamming coverage 0.547 +/- 0.0002



Evans, J.W. *Rev. Mod. Phys.*, **65**, No. 4, (1993)



same

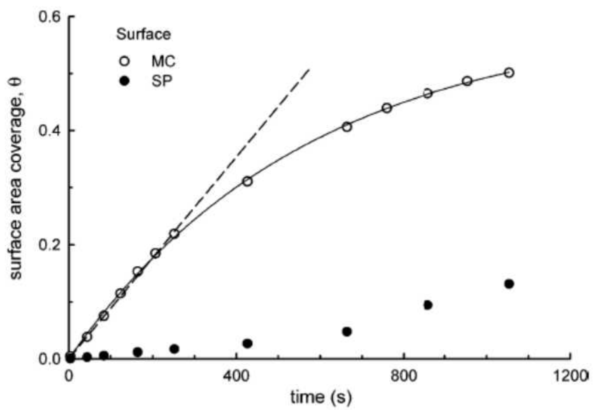
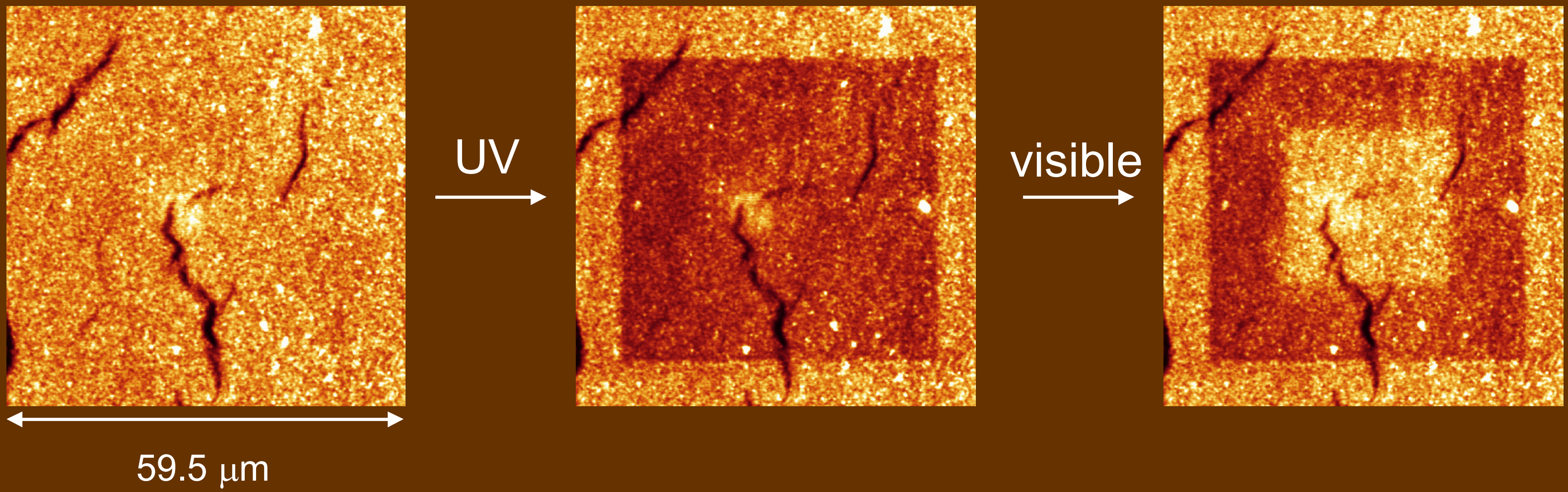


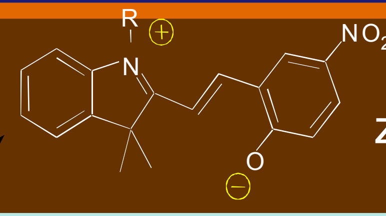
Figure 3. Plot of fractional surface coverage as a function of time for colloids depositing onto the photoswitched (MC) and unexposed (SP) regions of the substrate modified with an SP-*co*-MMA

M. Piech, M. C. George, N. S. Bell and P. V. Braun:, *Langmuir*, **22**, 1379-1382 (2006).

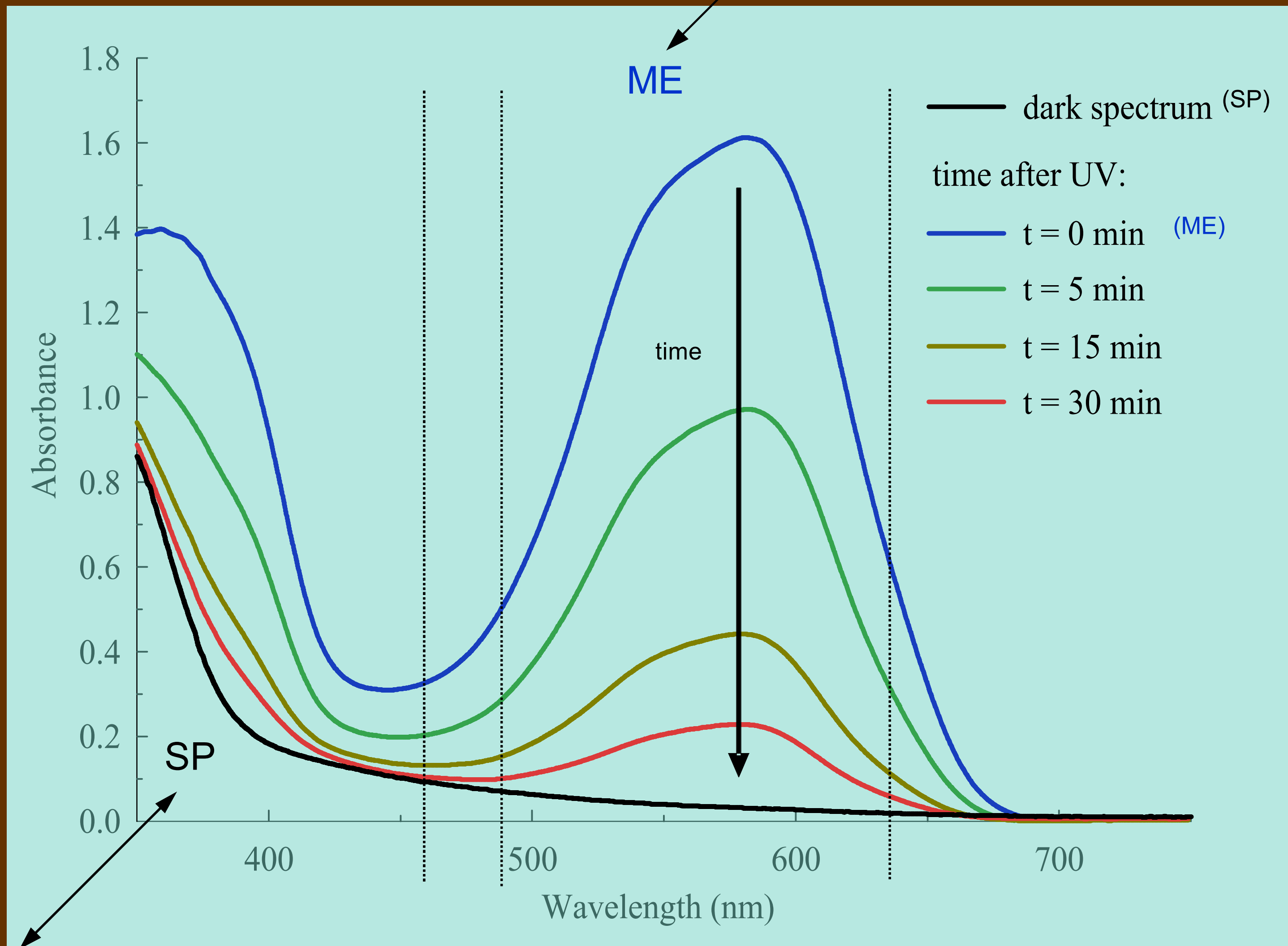
Reversible Switching

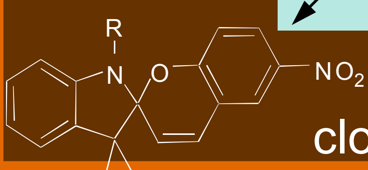


Absorbance spectrum of a complex fluid, containing SP/MMA copolymer



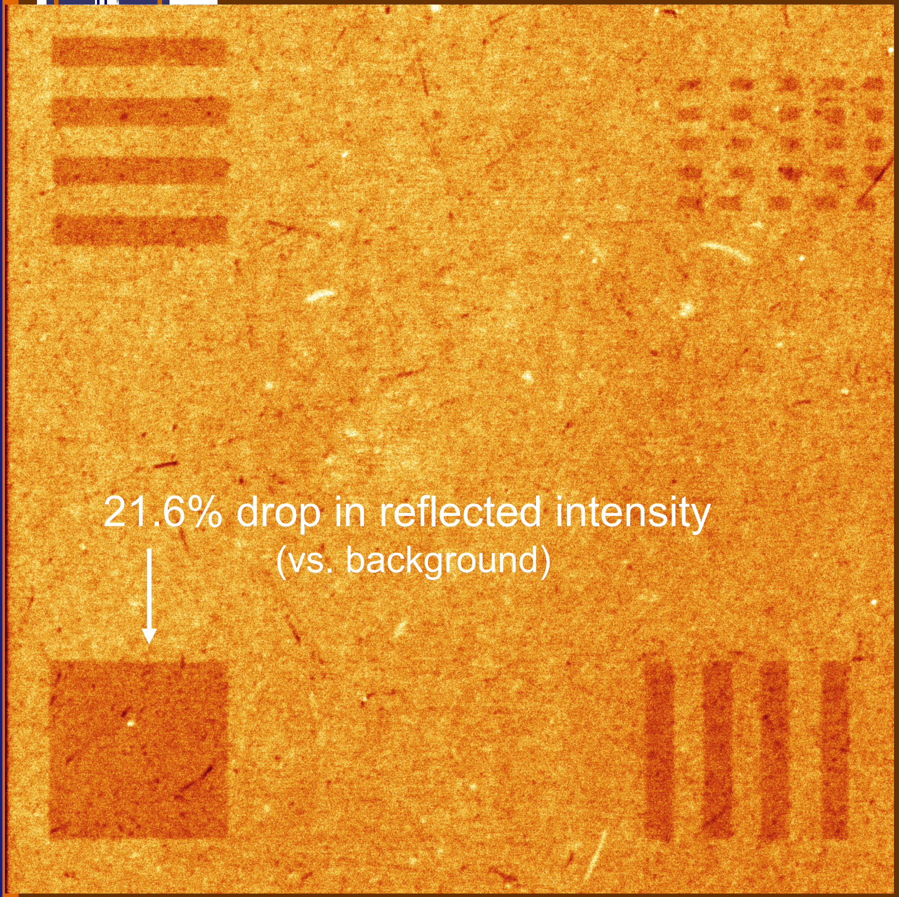
zwitterionic form



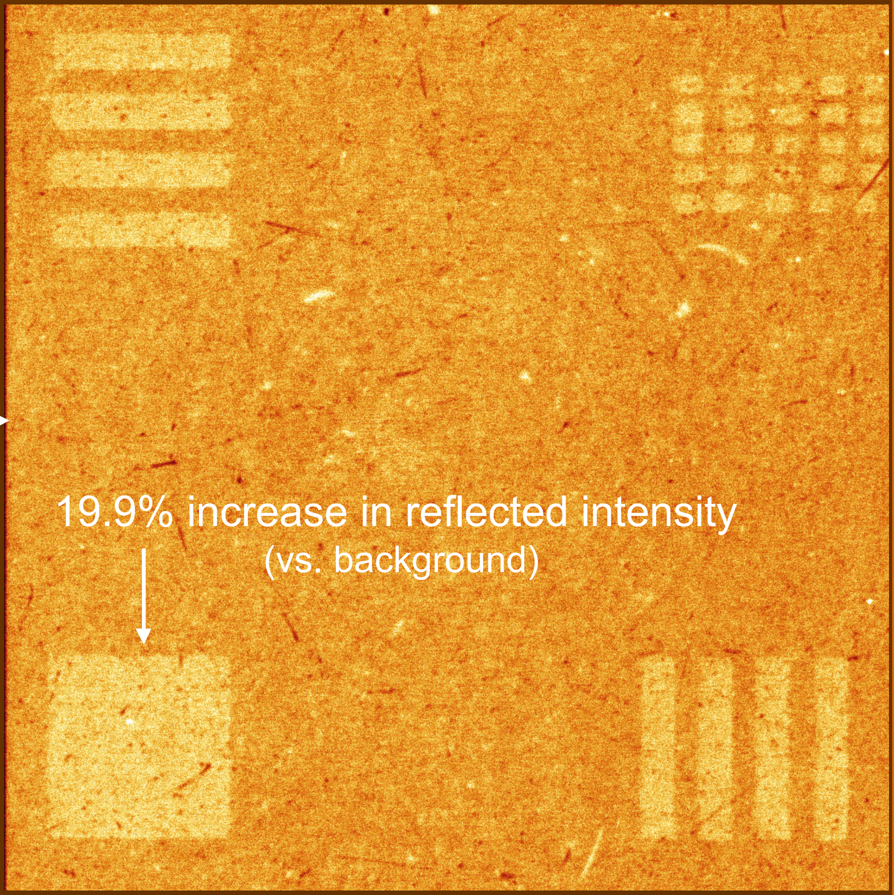


closed form

Confocal Reflectance Images (458nm)



time



Initial image taken after 2-photon exposure   After several minutes (& additional exposure)

- Initial drop in reflected intensity… followed by brightening with time !?!?!

Application III: Photo-induced phase transitions

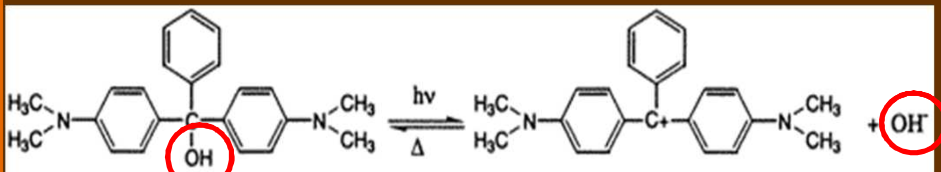


Photo-disassociating molecule

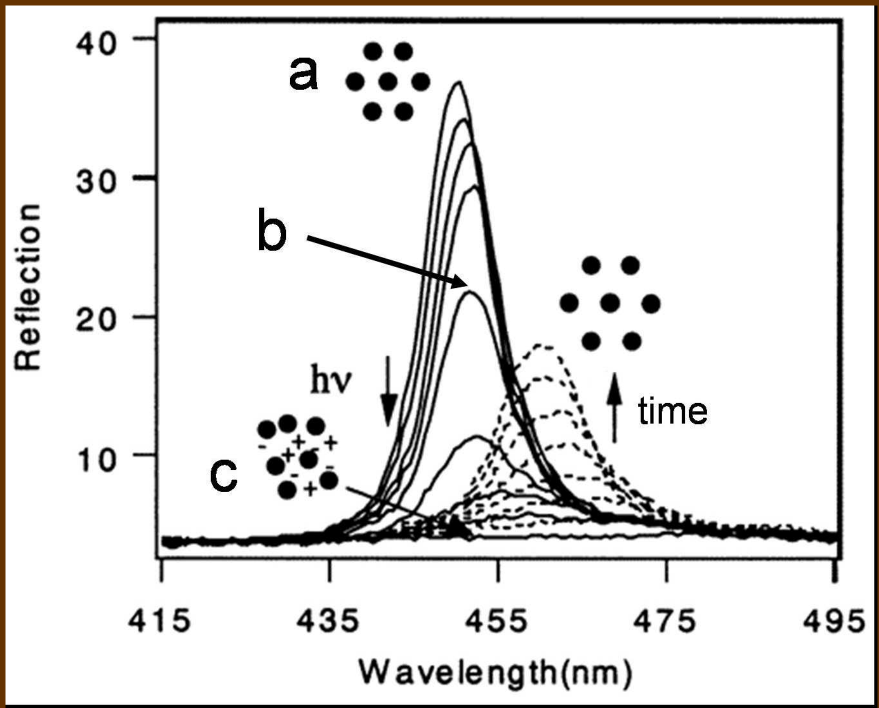
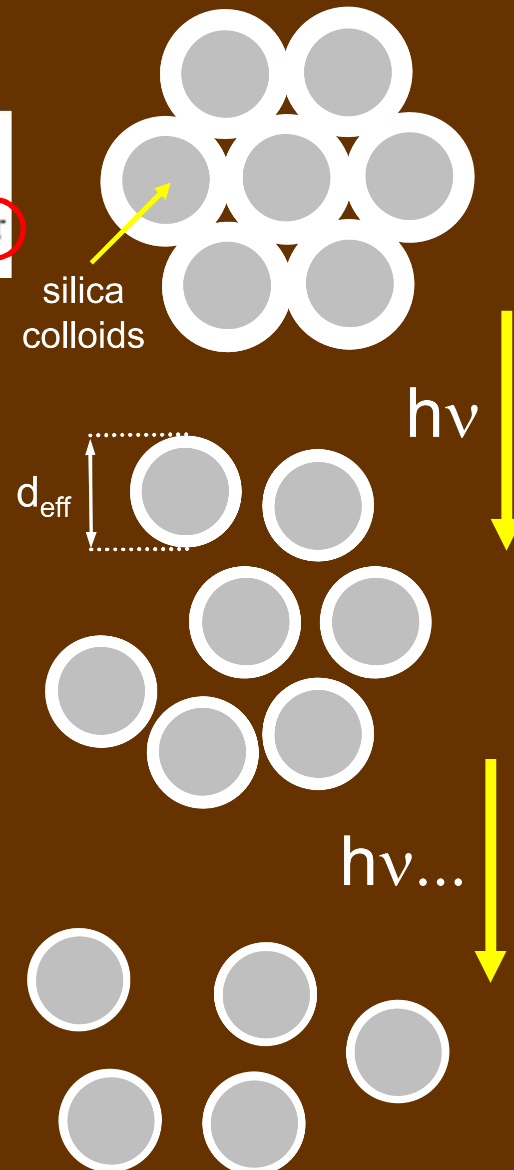
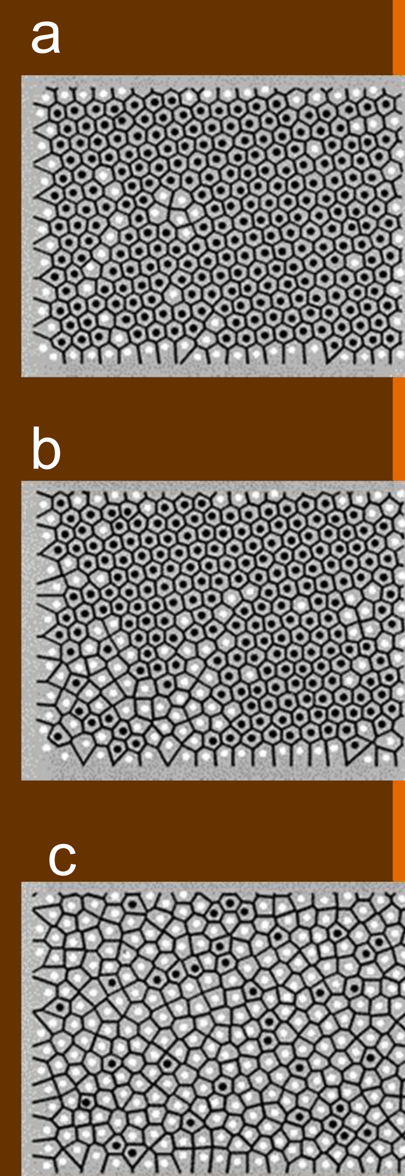


Photo-chemically induced melting
(& re-crystallization with different spacing)





Zhong-Ze Gu, Akira Fujishima, and Osamu Sato, "Photochemically Tunable Colloidal Crystals", *J. Am. Chem. Soc.* **122** (2000) 12387-12388.

Photo-induced phase transitions

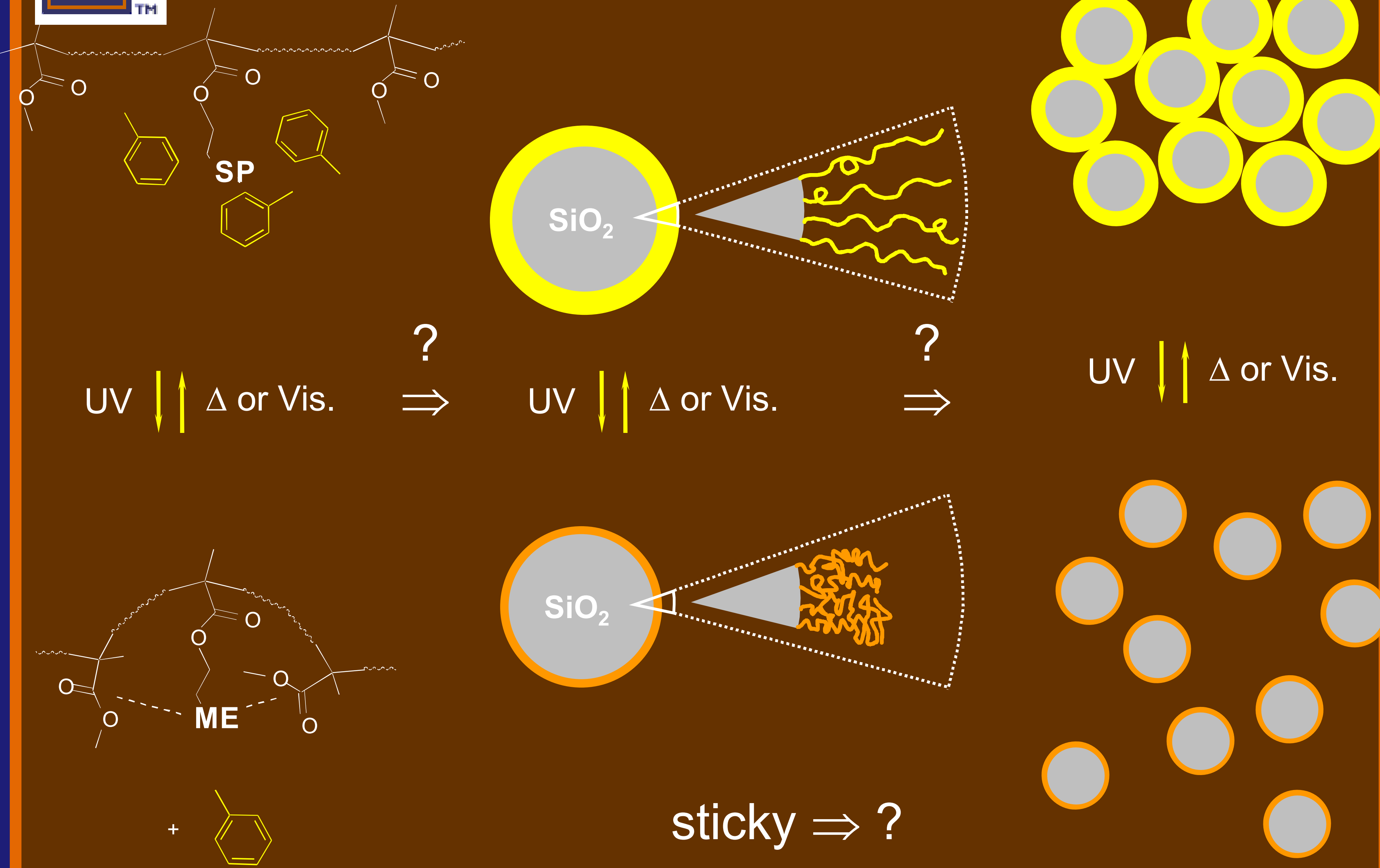
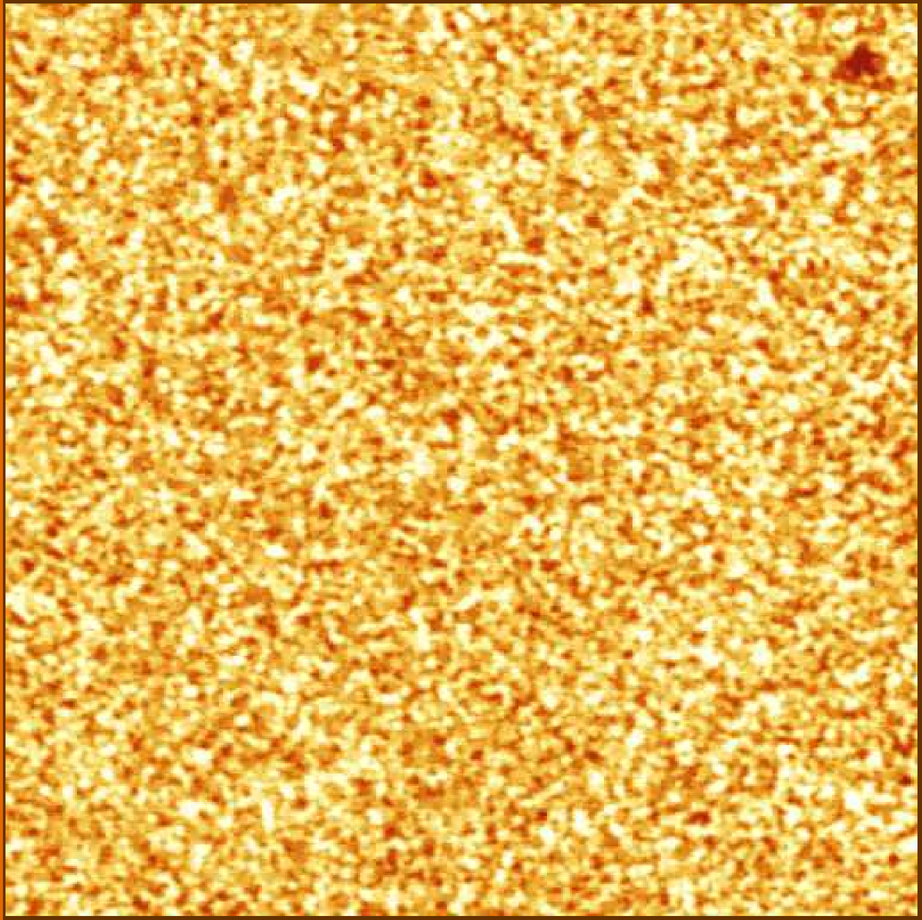


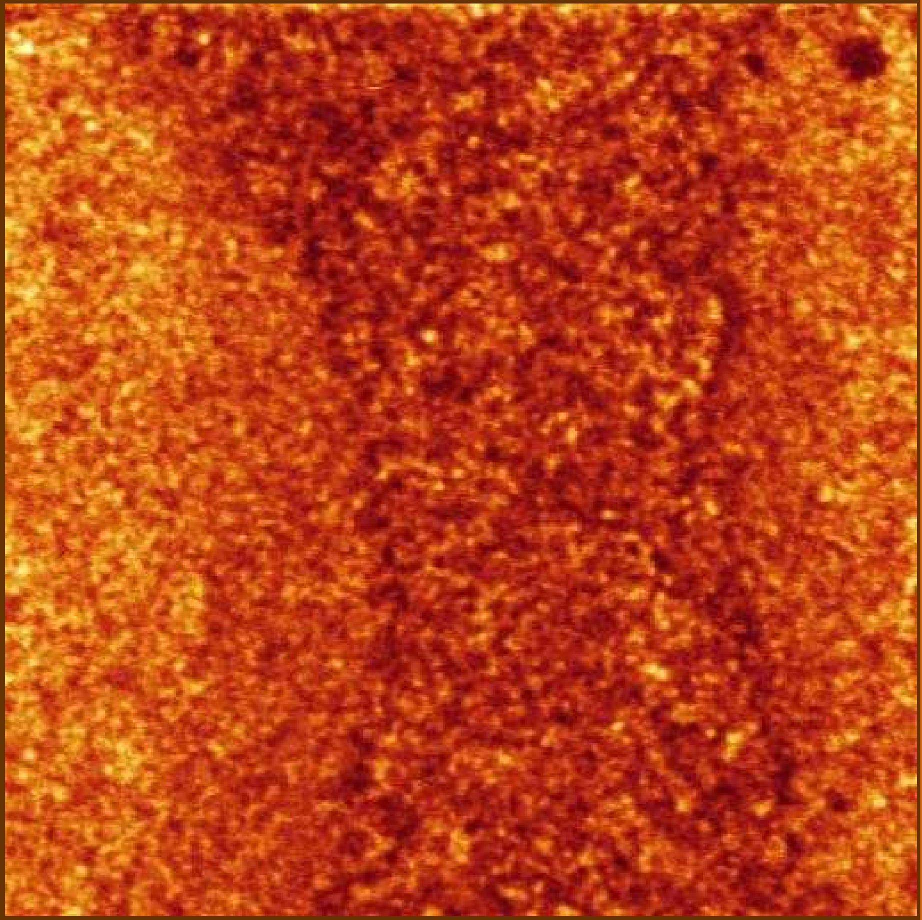
Photo-induced phase transitions

Confocal microscope series of xy scans.

Transient melting and revitrification ?

Problem: Colloids too sticky.

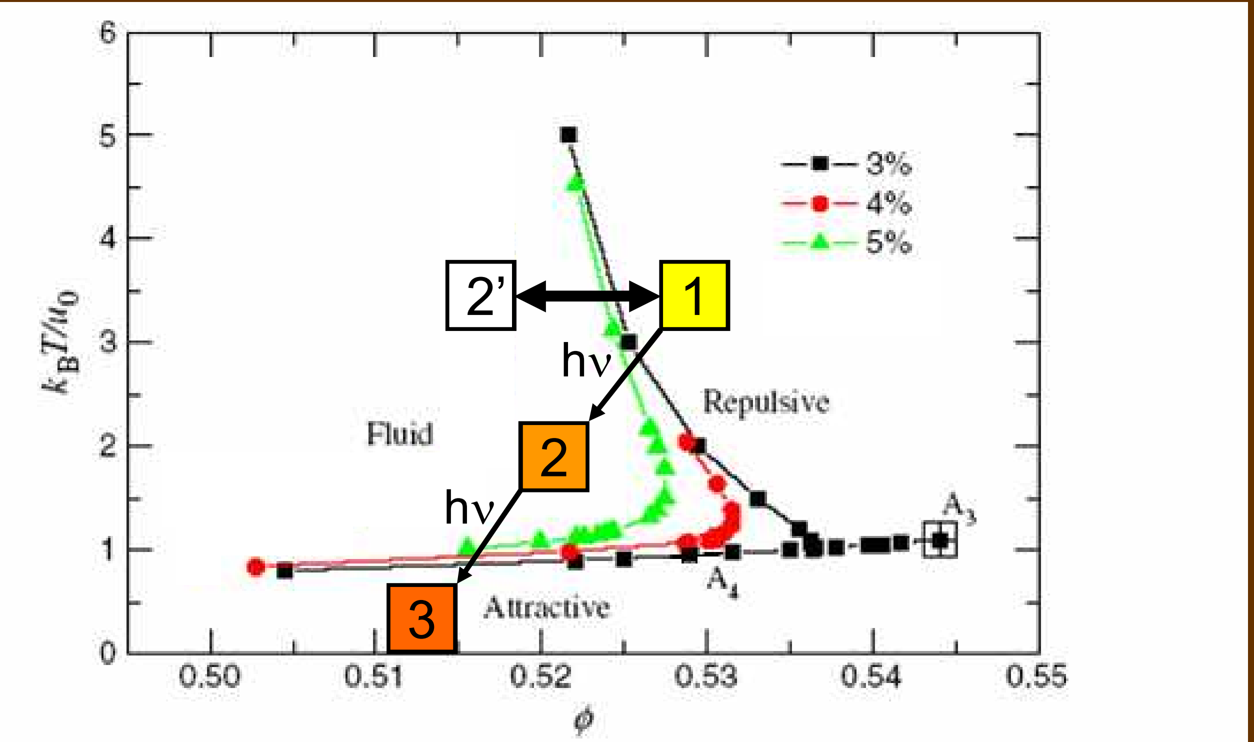




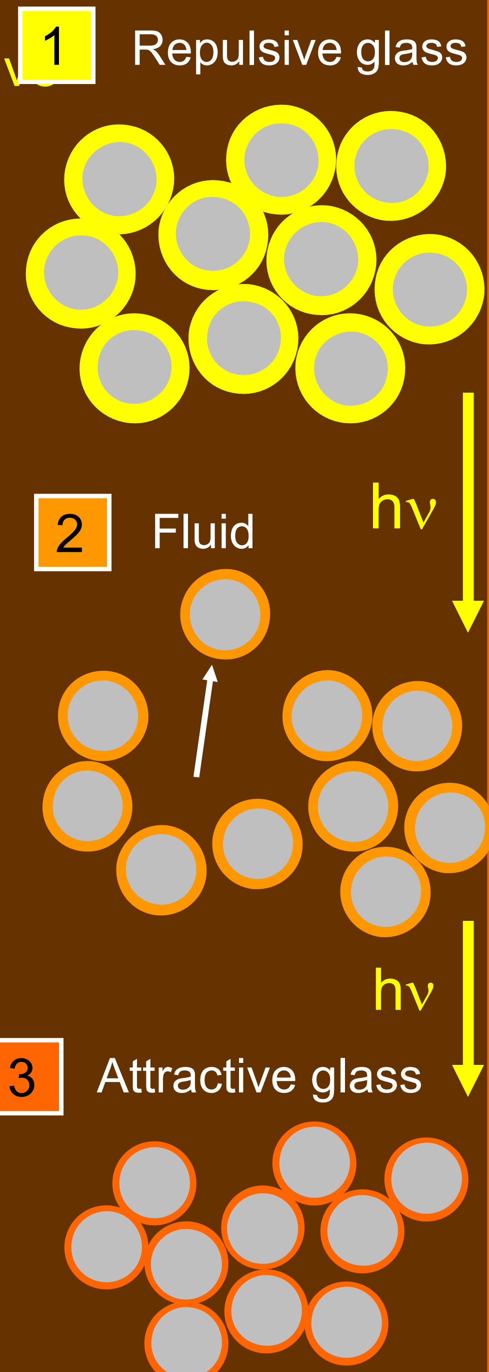
59.5 μm

283 nm Silica – 30nm SP/MMA Core-Shell Colloidal Sediment (wet with toluene).

Phase diagram for colloids with hard core repulsive and short range attractive square well potentials

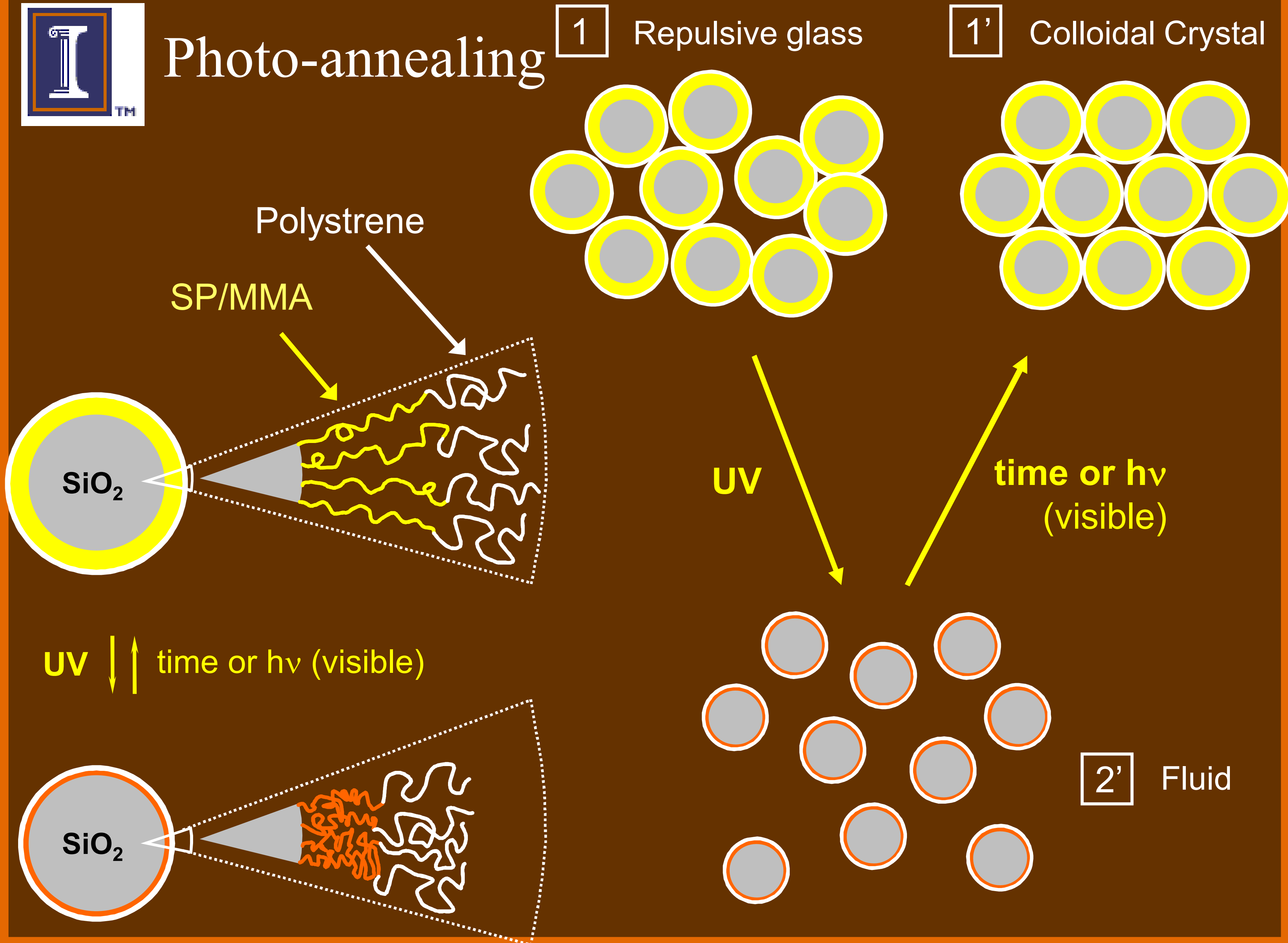


Solution: SP-co-MMA-block-PS
(colloids do not aggregate upon UV irradiation)



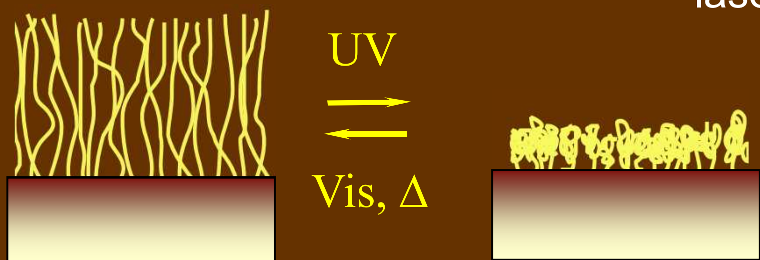
Luca Cipelletti and Laurence Ramos, "Slow dynamics in glassy soft matter", *J. Phys.: Condens. Matter* **17** (2005) R253-R285

Photo-annealing



Future Work

• Verify thickness change in grafted SP-MMA copolymer films

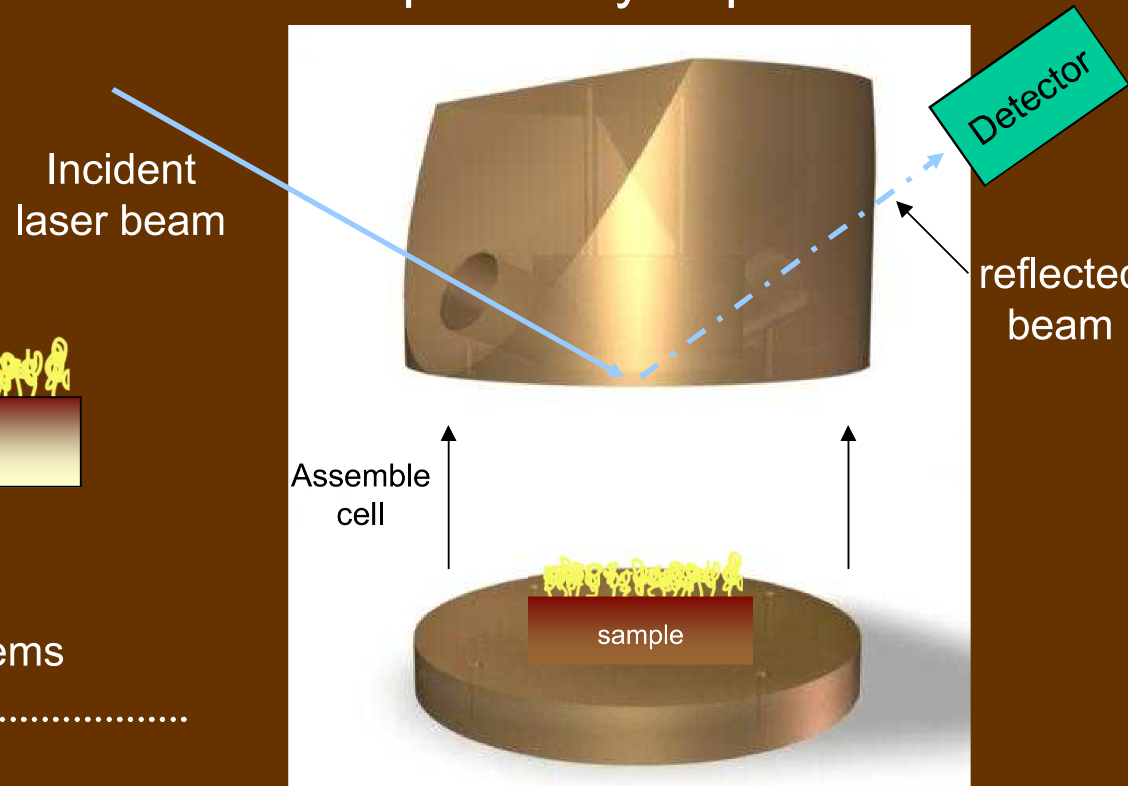


- AFM…
- Light Scattering – Inherent Problems

• Photo-annealing of colloidal crystals

• Knock off adsorbed particles with visible wavelengths

Ellipsometry Liquid Cell



Ellipsometry gives:

•thickness

•Refractive index