SAND2009-1617P

Interfacial Control in Photochromic Systems

Nelson S. Bell

Marcin Piech, United Technologies Corp.
Matt George and Paul Braun, UIUC
Greg Jamison, Chad Staiger, SNL
Anne Grillet, Chris Brotherton, Tim Koehler, SNL
Liu Jiang, Tim Long, John Lean

Sandia National Laboratories

Albuquerque, New Mexico 87185-0888

Sandia National Laboratories is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company.
This work was supported by the U.S. DOE under contract DE-AC04-94AL85000.

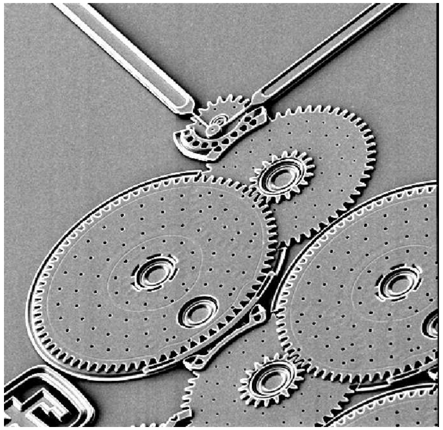
Sandia
National
Laboratories

Overview

- Photo-Responsive Surfaces and Fluid Motion
- Photo-Controlled Colloidal System
- Photo-physical effects in Colloids
- 2D and 3D Patterning with Colloids
- Optical Trapping of Photochromic Colloids

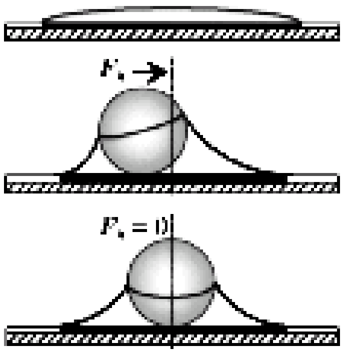
Motivation

Photochemical control of physical interaction processes on the molecular level



MEMS: ***tribology***

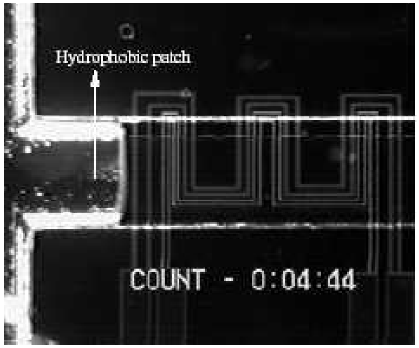
Nano-interaction management



Self-assembled nanostructures:

Microfluidics: ***rheology***

J. Micromech. Microeng.., 13, (2003), p. 261



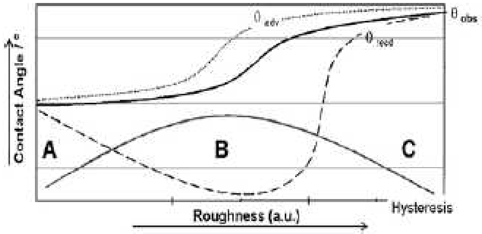


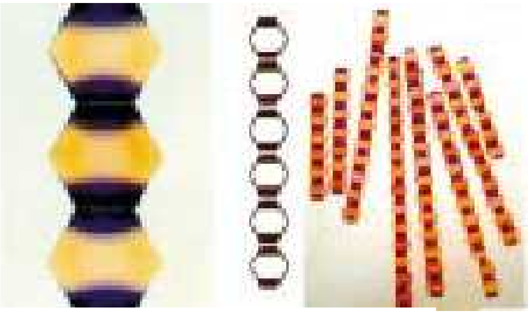
Figure 1. Wettability vs. roughness (schematically). (A) Smooth surface, (B) Wenzel Regime, (C) superhydrophobic surface. θ_{obs}: observable (static) c.a., θ_{adv}: advancing c.a., θ_{recd}: receding c.a.

J. Sol-Gel Sci. Tech., 26, (2003), p.789

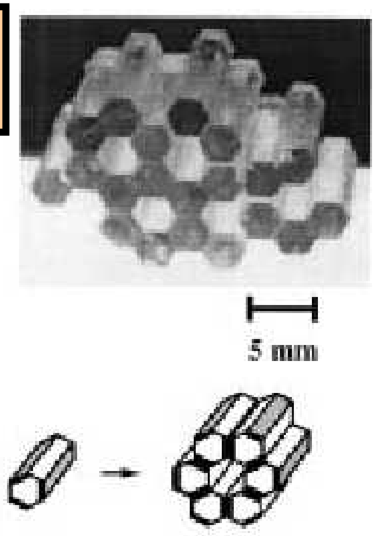
- **Fundamental competency for the realization and application of high-surface-area microsystem architectures and the controlled fabrication and utilization of nanostructured materials**

Heterogeneous Particle Assembly

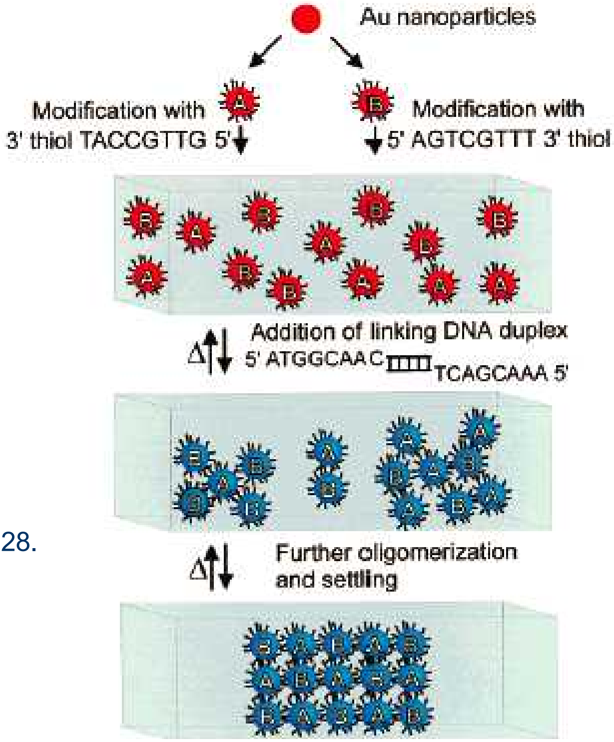
Are there analogs to directed assembly at the colloidal scale?



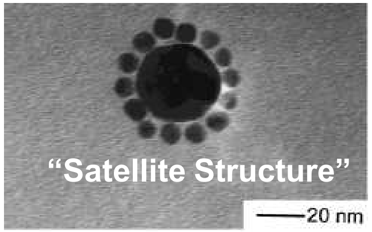
Ned Bowden, et al. *J. Am. Chem. Soc.* **121** (1999) 5373-5391



S.R.J. Oliver at al. *J. Colloid Interface Sci.*, **224** (2000) 425-428.



* Chad Mirkin, *Inorg. Chem*. 39 (2000)
Hiddessen et al. *Langmuir*, 16 (2000)

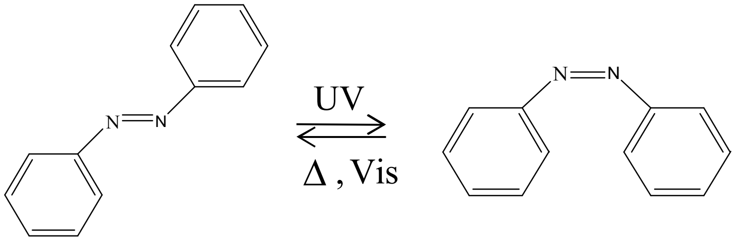


There are novel systems to study with these methods…

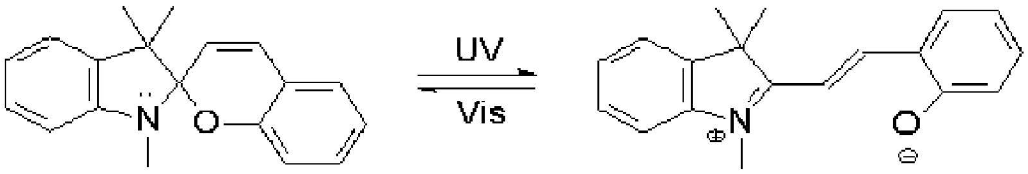
- Electrostatic Assembly (i.e. Ionomeric Gel).
- Photosensitive stabilization mechanisms or bonding.
  (Zaitsev SY, et al. Supramolecular Science, **4** (1997) 519-524.)
- Biological Surface Recognition*
  DNA, nucleotides, peptides, lipids …
    Observed structures include colloidal micelles, clusters, rings, and chains.
- Structured layer deposition using non-spherical particles
  (Choi et al. Langmuir (2000) **16**, 2997-2999.)

Photochromic Molecules

- Azobenzene



- Spiropyran

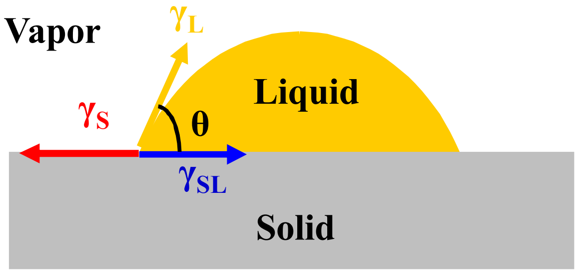


The dipole moment of these molecules are reversible, and monitored by:

- changes in optical profile (UV/Vis spectrum)

- alteration of surface energy (contact angle measurements)

Modeling of Surface Energy from Contact Angle Measurements



Young's equation

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta$$

Van Oss theory

$$\gamma_S = \gamma_S^{LW} + \gamma_S^{AB}$$

$$\gamma_S^{AB} = 2\sqrt{\gamma_S^{-}\gamma_S^{+}}$$

$$\gamma_L(1+\cos\theta) = 2(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{-}\gamma_L^{+}} + \sqrt{\gamma_S^{+}\gamma_L^{-}})$$

Surface energy separated into dispersive (LW), electron donating (-) and electron accepting (+) components

Van Oss Modeling of Azobenzene Surfaces

Azobenzene modified surface energy (mJ/m^2) was calculated by using three fluids of known dispersive, acid and base components.

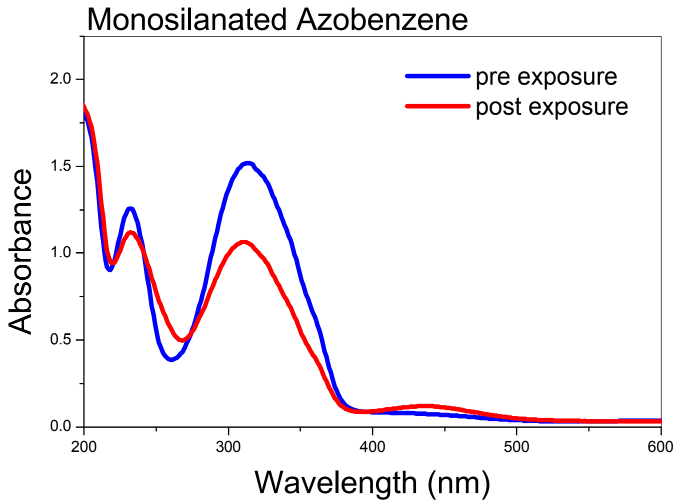
$$\gamma_L(1+\cos\theta) = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{-}\gamma_L^{+}} + \sqrt{\gamma_S^{+}\gamma_L^{-}}\right)$$

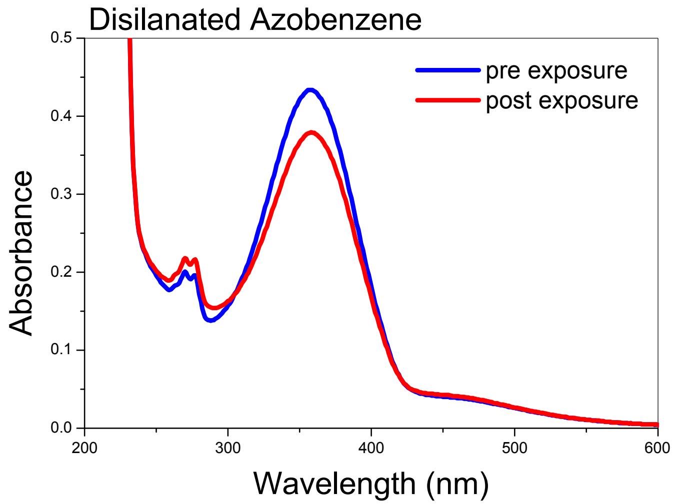
Table: Surface tensions and components of probe liquids (mJ/m^2) suggested by Van Oss

Liquid	γ_L	γ_L^{LW}	γ_L^{-}	γ_L^{+}	γ_L^{AB}
Polar					
DI water	72.8	21.8	25.5	25.5	51.0
ethylene glycol	48.0	29.0	47.0	1.92	19.0
formamide	58.0	39.0	39.6	2.28	19.0
Nonpolar					
diiodomethane	50.8	50.8	--	0	0
1-bromonaphthalene	44.4	44.4	0	0	0

Van Oss Modeling of Azobenzene

Contact Angle Measurements using three fluids of known dispersive, acid and base character.



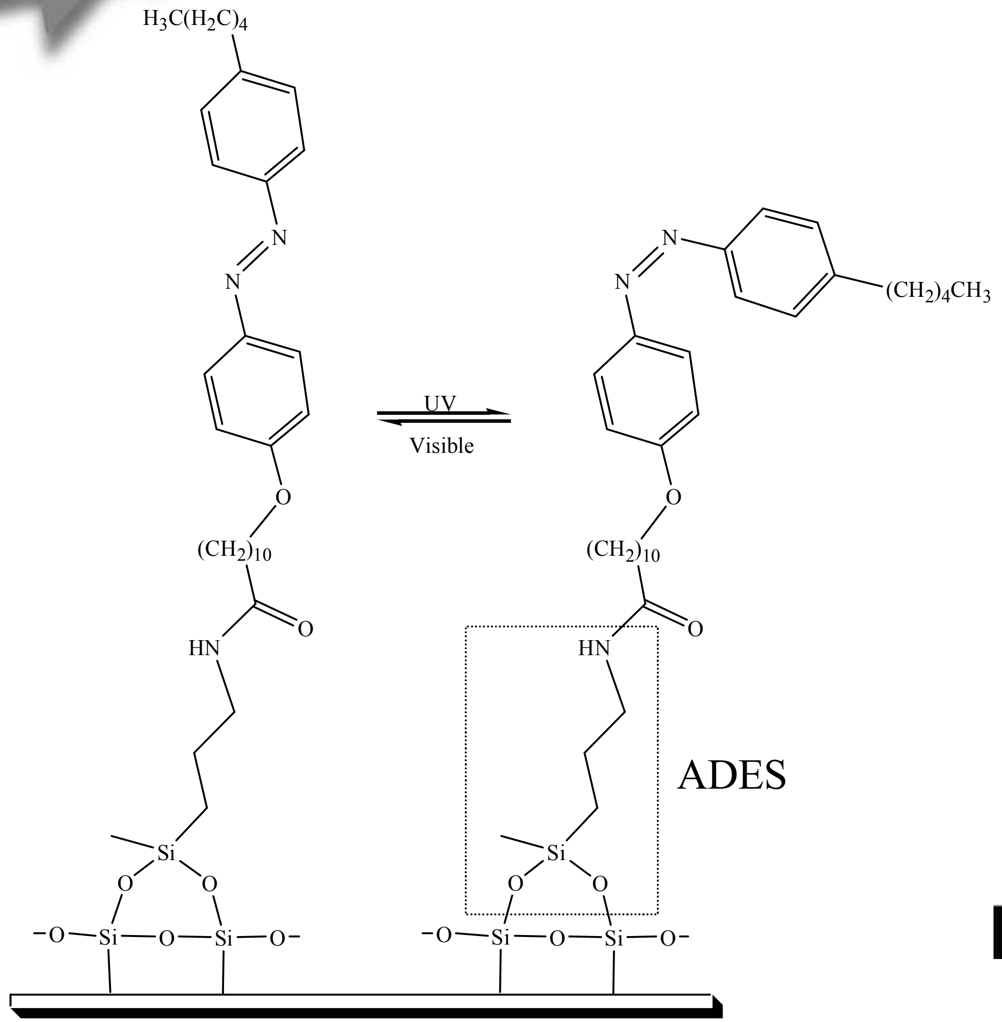


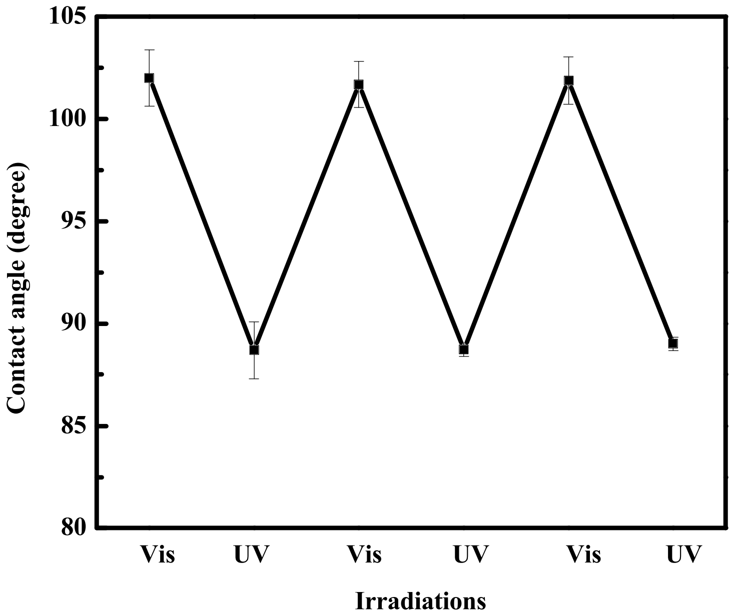
Solvent Parameters	σL	σD	σ-	σ+
Water	72.8	21.8	25.5	25.5
Diiodomethane	50.8	50.8	0	0
Formamide	58.2	39	39.6	2.28

$$\sqrt{(\sigma_l^D)(\sigma_s^D)} + \sqrt{(\sigma_l^-)(\sigma_s^+)} + \sqrt{(\sigma_l^+)(\sigma_s^-)} = \frac{\sigma_l(Cos\Theta + 1)}{2}$$

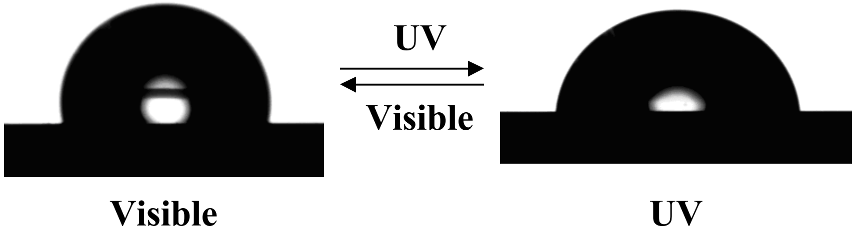
Azobenzene (Monosilanated)	σ^D	σ^+	σ^-
Unexposed	40.08	0.10	1.23
Exposed	40.44	0.07	7.89
Azobenzene (Disilanated)			
Unexposed	29.10	0.02	7.24
Exposed	29.44	0.95	7.15

Surface Design with Azobenzene





Wetting angle



Visible	UV
100°-102°	88°-90°

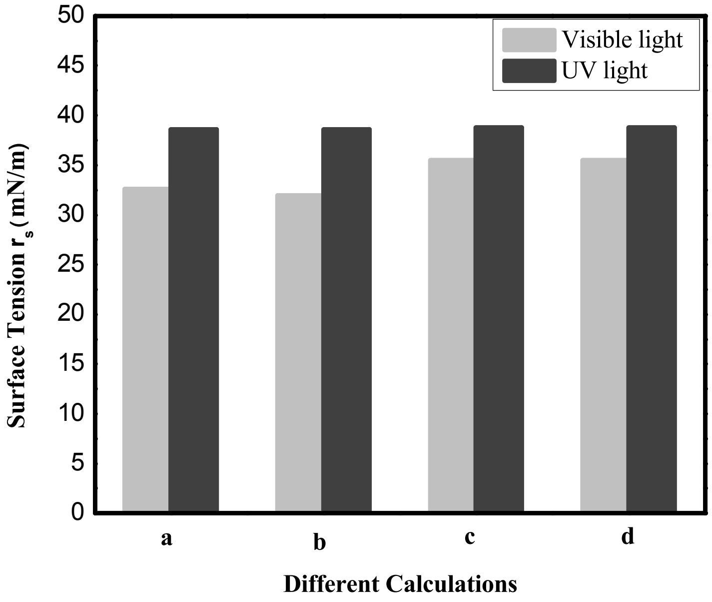
Azobenzene molecules attach to the surface through aminopropylmethyldiethoxysilane(ADES)

D. Yang et al. *Langmuir*, **2007**, *23*, 10864-10872.

Van Oss Modeling of Azobenzene Surfaces

Azobenzene modified surface energy (mJ/m^2) was calculated by using three fluids of known dispersive, acid and base components.

$$\gamma_L(1+\cos\theta) = 2(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{-}\gamma_L^{+}} + \sqrt{\gamma_S^{+}\gamma_L^{-}})$$



Calculations	Illumination	γ_S^{LW}	$(\gamma_S^{+})^2$	γ_S^{-}	γ_S
a)	Visible	32.59	-0.09	0.42	32.59
	UV	38.59	-0.21	3.23	38.59
b)	Visible light	32.02	-0.69	1.99	32.02
	UV	38.59	-0.55	4.57	38.59
c)	Visible	35.49	-0.28	0.36	35.49
	UV	38.83	-0.22	3.22	38.83
d)	Visible	35.49	-1.00	2.07	35.49
	UV	38.83	-0.57	4.58	38.83

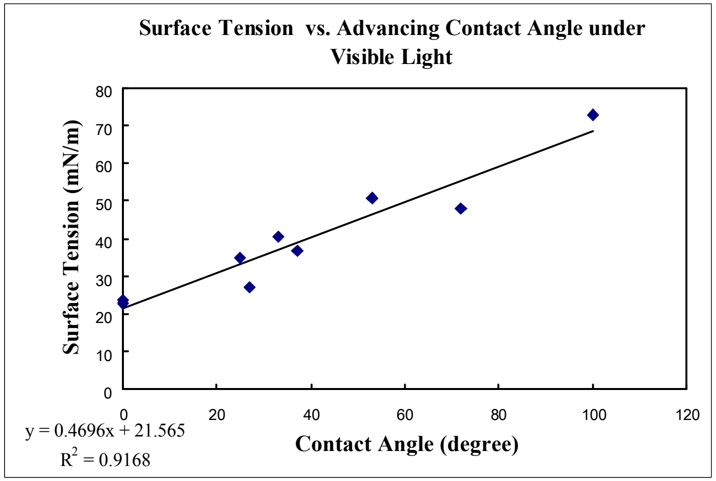
a) Using DI water, Ethylene glycol, diiodomethane to calculate; b) Using DI water, Formamide, diiodomethane to calculate; c) Using DI water, Ethylene glycol, 1-Bromonaphtalene to calculate; d) Using DI water, Formamide, 1-Bromonaphtalene to calculate

Contact Angle Measurement with Liquids

Table: Contact angle on azobenzene modified surface with various solvents (degree).

Solvents	trans	cis	Surface Tension (mN/m)	Switching Angle ($\theta^{trans}_{adv} - \theta^{cis}_{adv}$)
	θ_{adv}	θ_{adv}		
acetonitrile	27.0±0.55	11.5±0.87	27	15.5
benzonitrile	32.0±2.0	17.0±0.76	38.65	15
DI water	101.3±0.98	88.9±0.86	72.8	12.4
diiodomethane	54.1±0.49	42.1±1.08	50.8	12
dimethylformamide	37.5±1.74	26.8±0.53	36.8	10.7
formamide	82.2±1.36	71.5±0.66	58.2	10.7
1-methylnaphthalene	33.3±1.09	23.3±0.34	40.5	10
ethylene Glycol	73.2±0.73	63.9±0.71	48	9.3
1-bromonaphthalene	38.0±0.67	29.7±0.40	44.4	8.3

Linear relationship between surface tension of solvents and its contact angle on azobenzene surface



Droplet Mobility Requirements

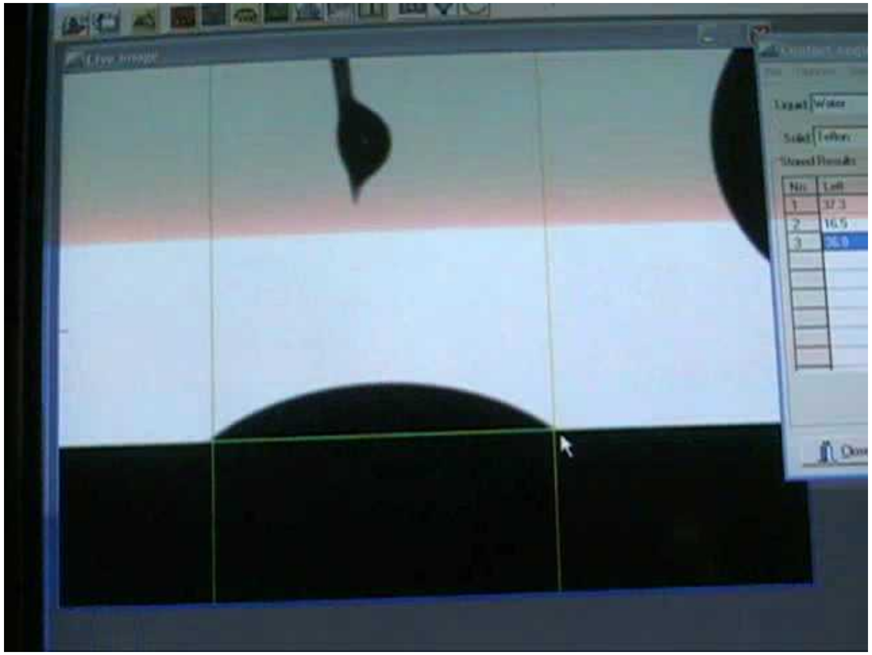
Requirement: The receding contact angle (trans-isomer) under visible light must be larger than advancing contact angle (cis-isomer)

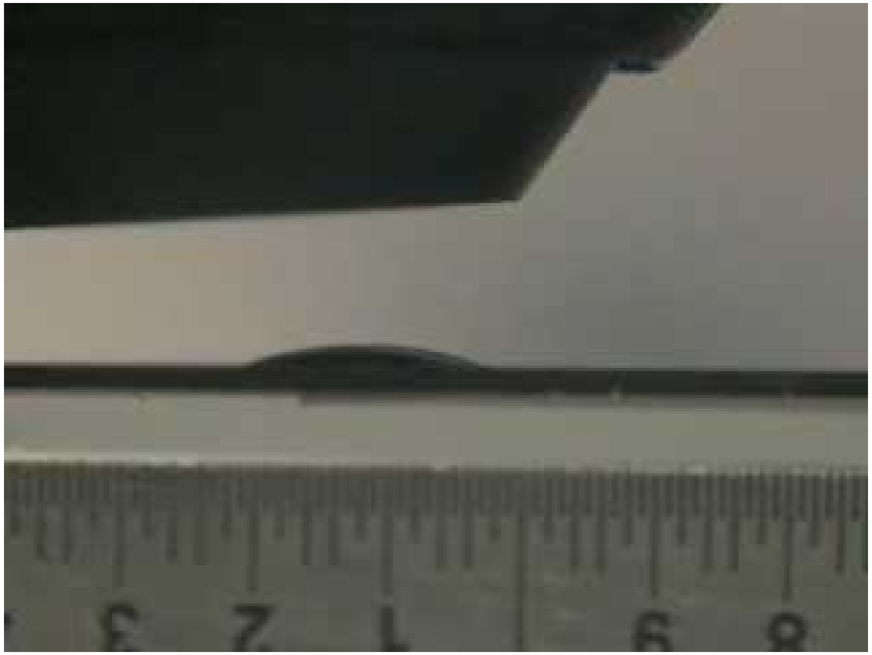
Table: Contact angle measurements (degree) on azobenzene modified surface with various solvents.

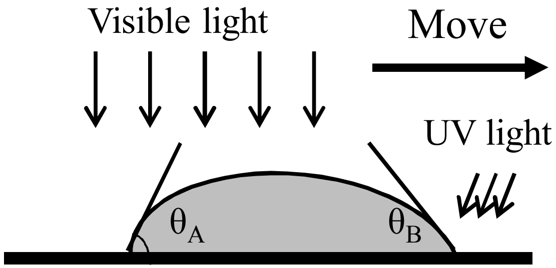
Liquid	trans		cis	
	θ_{adv}	θ_{rec}	θ_{adv}	θ_{rec}
Fulfill motion requirement				
benzonitrile	32.0±2.0	26.2± 1.25	17.0± 0.76	--
diiodomethane	54.1± 0.49	43.7± 0.58	42.1± 1.08	33.1± 1.28
dimethylformamide	37.5± 1.74	29.6± 1.47	26.8± 0.53	19.0± 1.34
1-bromonaphthalene	38.0± 0.67	33.5± 0.5	29.7± 0.40	24.6± 0.51
acetonitrile	27.0± 0.55	19.4± 1.41	11.5± 0.87	--
1-methylnaphthalene	33.3± 1.09	23.5± 0.77	23.3± 0.34	13.5± 0.56
Not fulfill motion requirement				
DI water	101.3± 0.98	76.0± 2.0	88.9± 0.86	69.8± 1.4
formamide	82.2± 1.36	62.8± 1.18	71.5± 0.66	58.2± 1.01
ethylene glycol	73.2± 0.73	49.0± 1.15	63.9± 0.71	41.5± 0.49

Motion of 1-Bromonaphthalene by UV Light

We demonstrate the idea of using light to move liquids on a photoresponsive surface.







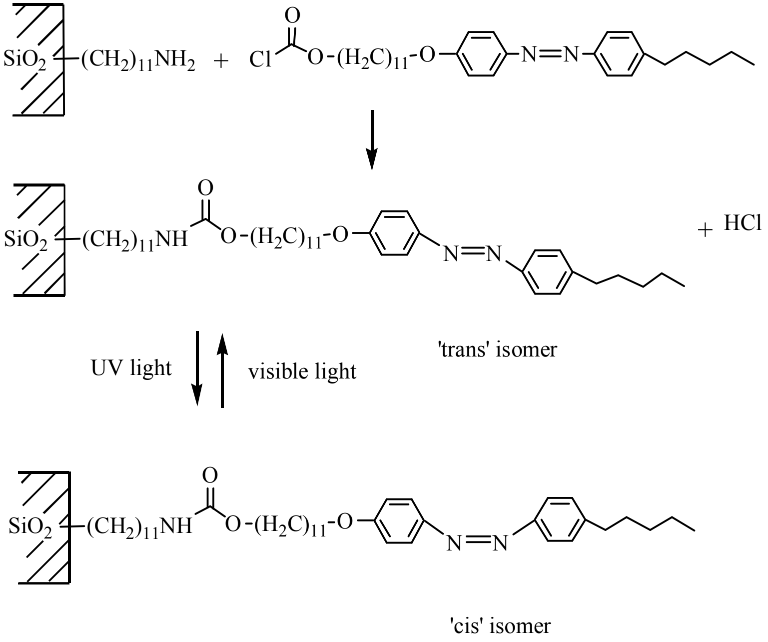
Interfacial Energy Calculation

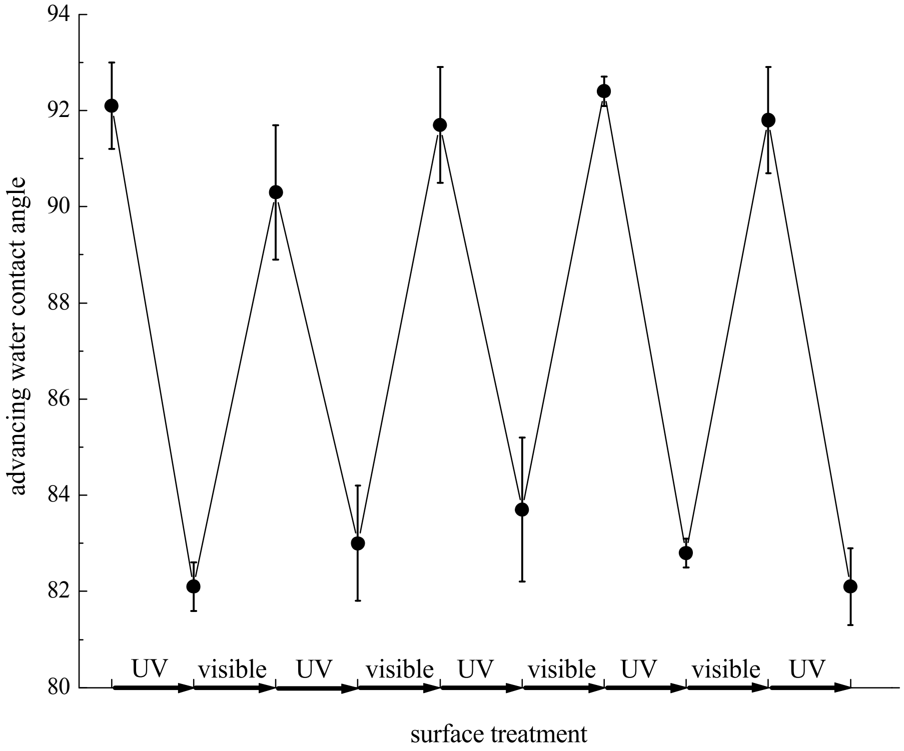
A transition from negative to positive interfacial energy is desired for photo control of wetting characteristics.

$$\Delta G_{131} = -2\left(\sqrt{\gamma_1^D} - \sqrt{\gamma_3^D}\right)^2 - 4\left(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_3^+\gamma_3^-} - \sqrt{\gamma_1^+\gamma_3^-} - \sqrt{\gamma_3^+\gamma_1^-}\right)$$

	Pre exposure	Post Exposure	Change in Surface Energy
Cyclohexane	-4.69	-7.03	-2.34
Chloroform	2.72	13.51	10.78
Tetrahydrofuran	-12.29	-16.31	-4.02
Diiodomethane	-2.67	-3.83	-1.16
Water	-80.14	-49.41	30.73
Formamide	-24.77	-17.46	7.31
Glycerol	-43.54	-33.54	10.00
Ethylene Glycol	-26.37	-20.52	5.85

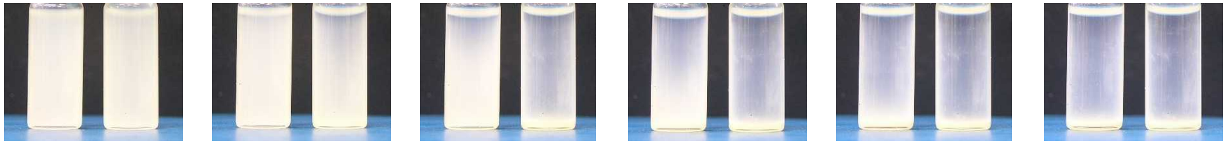
Azobenzene Derivatized Surface and Colloid Aggregation Response





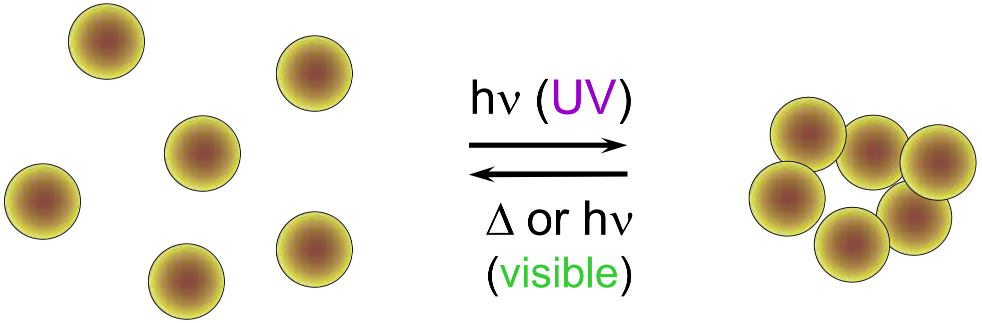
Left sample is visible exposed
Right sample is UV exposed

Sedimentation Rate Difference

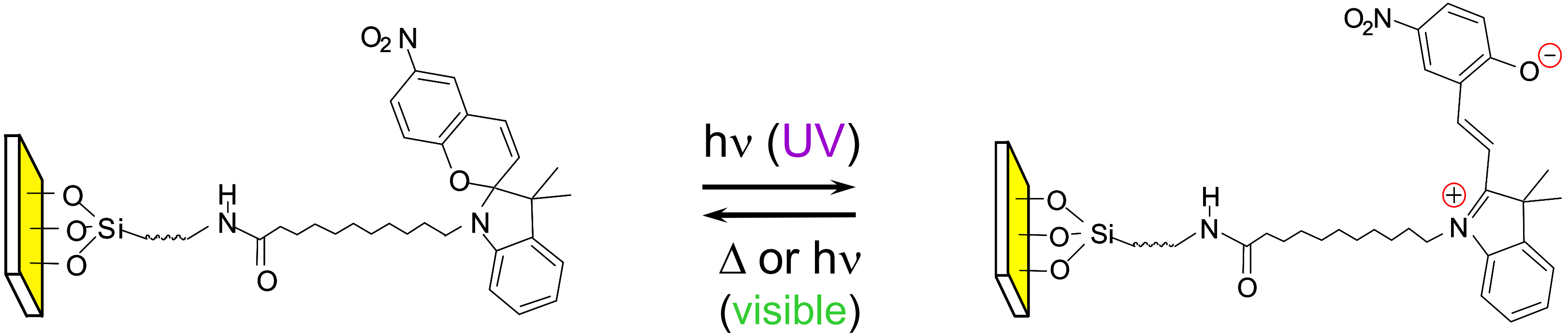


12 sec 60 sec 120 sec 180 sec 240 sec 300 sec

Reversible Light-regulated Colloidal Interactions



Approach: Utilize reversible photochemical reaction



closed form

Spirobenzopyran (SP)

zwitterionic form

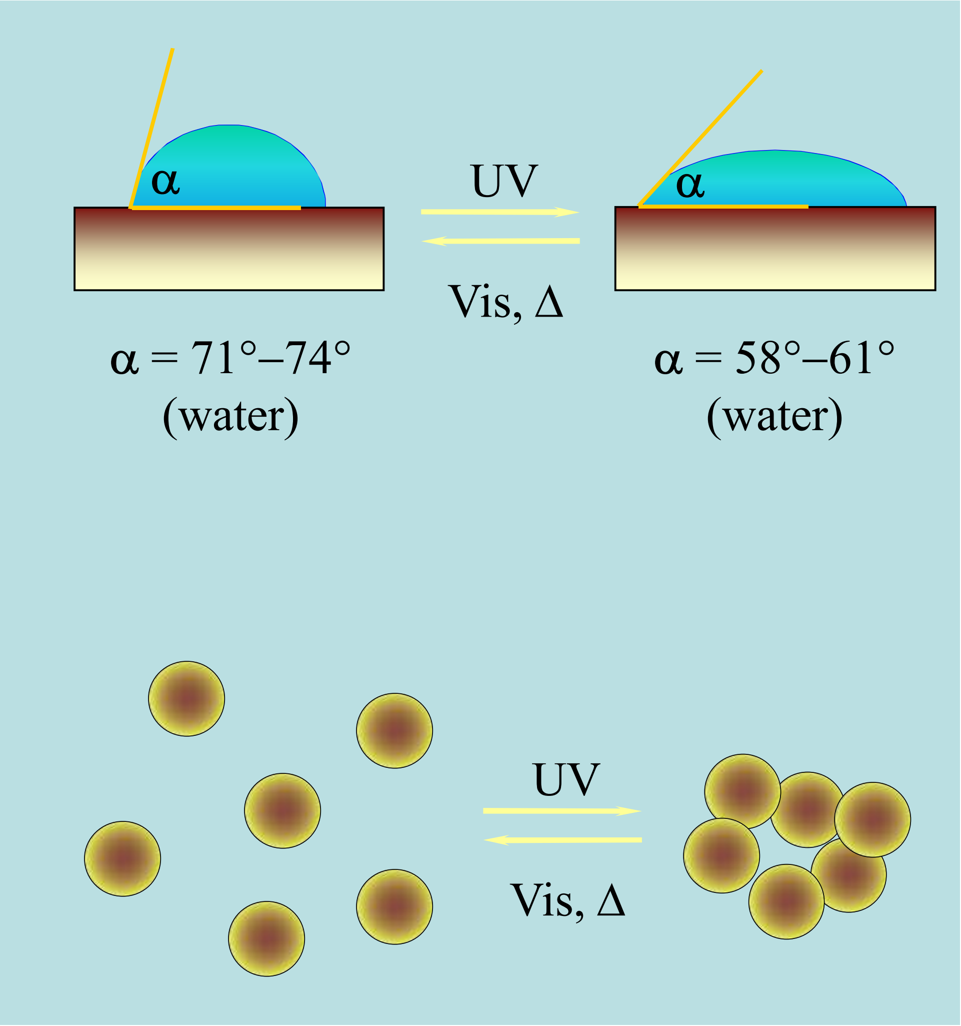
Merocyanine (ME)

- Reversible aggregation of SP-coated colloidal particles in non-polar solvents

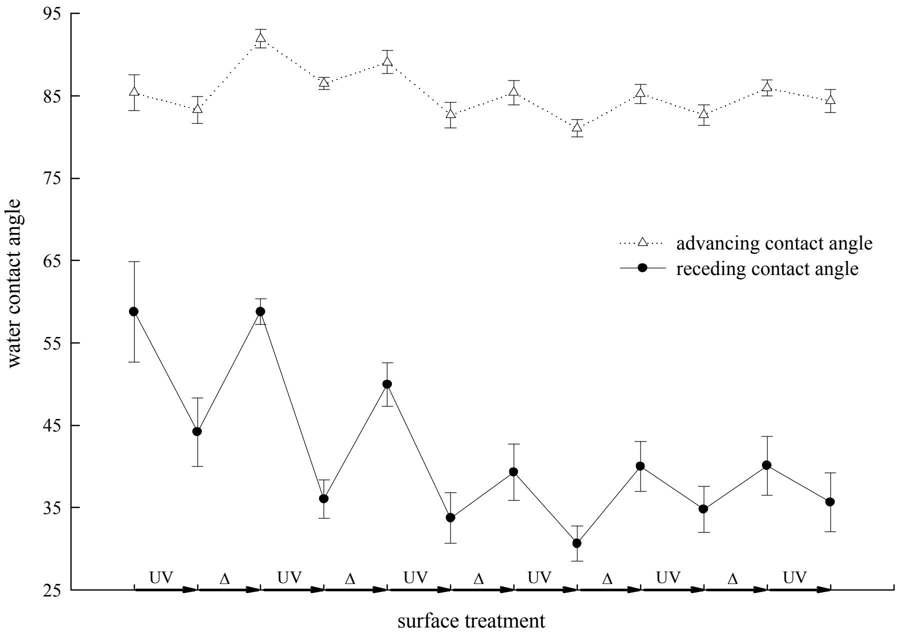
  K. Ichimura, et al. *J. Mat. Chem.* **4**, 883 (1994)

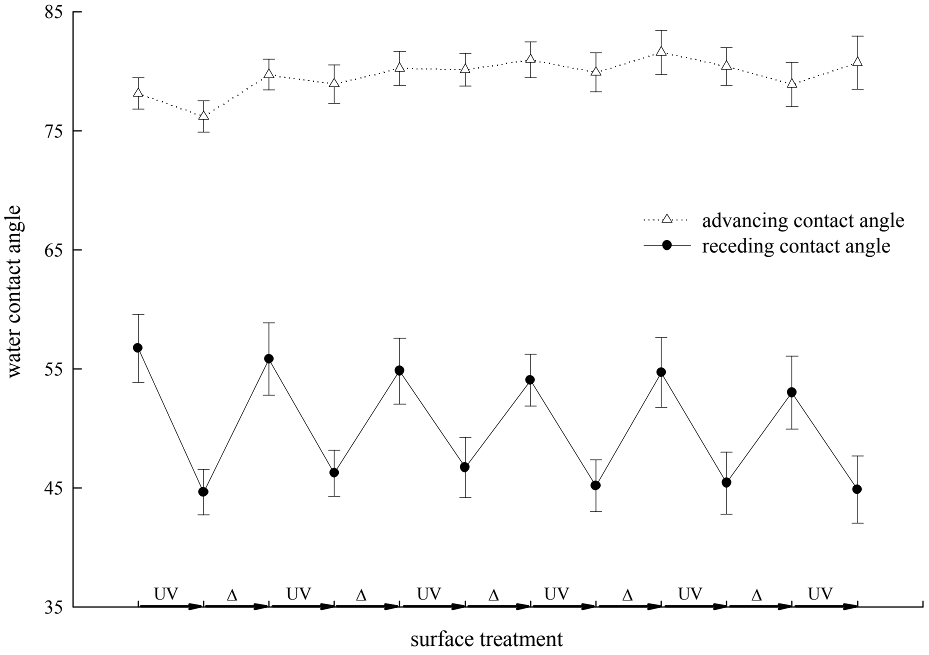
Effects of Photo-Isomerization on Spiropyran Monolayers

- Spyrobenzopyran monolayers on flat surfaces demonstrate reversible wettability change
- Contact angle altered by as much as 13° (Garcia, *et al.*)
- Colloidal particles covered with SP monolayers and dispersed in non-polar solvents undergo reversible aggregation (Ichimura, *et al.*)
- Change brought about by marked polarity difference between closed SP and open ME forms



Wetting of SPMMA monolayers versus SPMMA-*co*-MMA (20% SP) polymers





✓ Loss of switching ability is prevented by using polymeric layers instead of organic monolayers.

Strategic Approach to forming a Photosensitive Colloidal System

Goal: Demonstrate Reversible aggregation and dispersion of colloidal particles by photochromic effects.

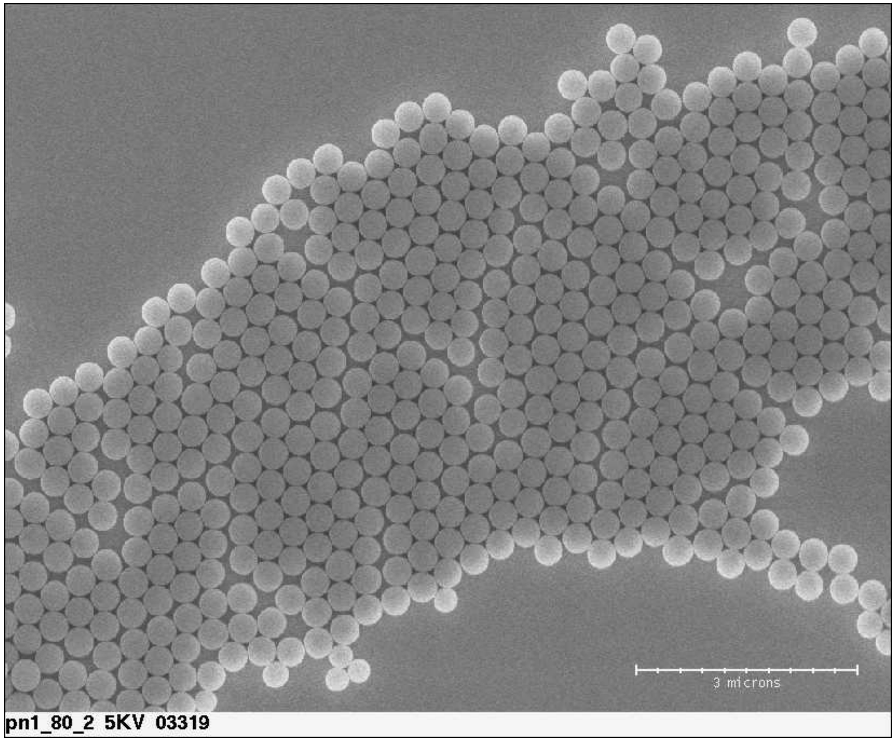
Particle system: Silica

- monodisperse,
- spherical
- common model system
- surface chemistry can be modified using silanes

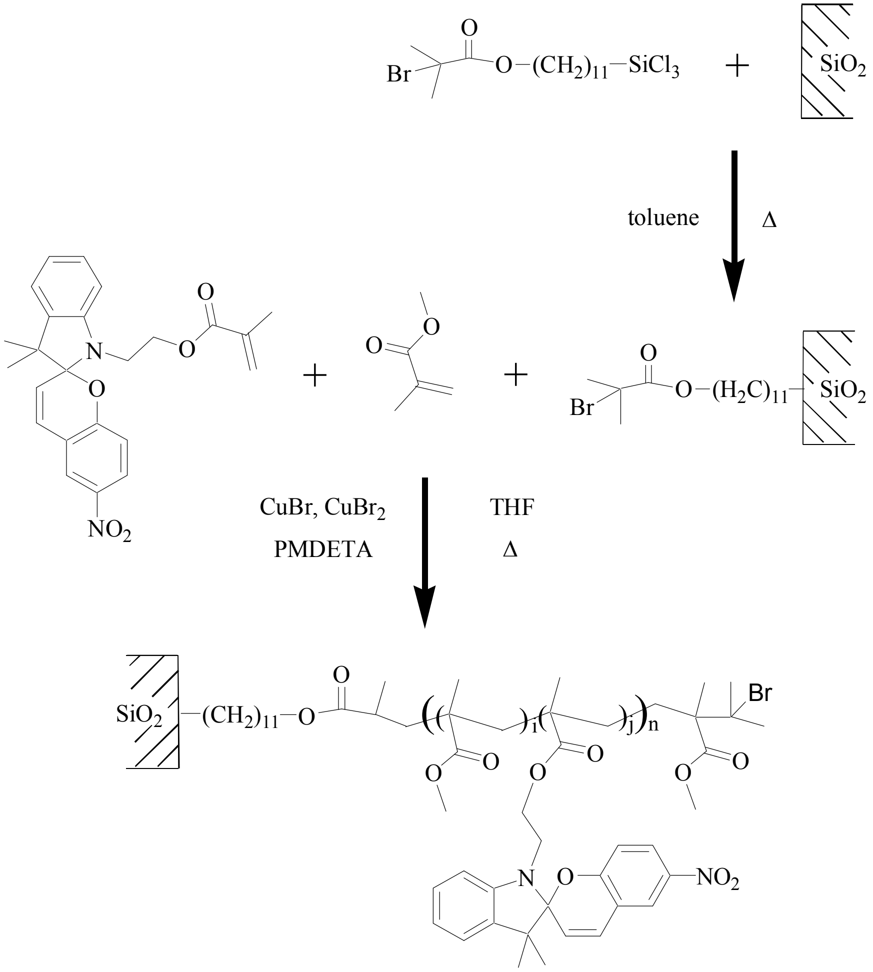
Organic component: spiropyran

- large dipole moment change
- forms a zwitterionic state
- literature states solubility changes of SPMMA polymers in nonaqueous solvents

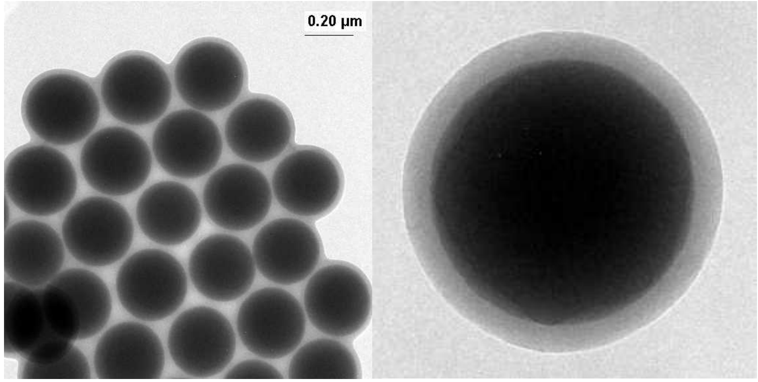
Approach: derivatize particles with layers of photo-switchable polymer.



Preparation of photo-responsive colloids



- Prepared silica particles modified with monolayer of photo-active spirobenzopyran (SP) molecules
- Colloids demonstrated photo-aggregation in selected solvents (*e.g.*, toluene).
- However, monolayer degradation and photo-bleaching limited their applicability
- Used Atom-Transfer Radical Polymerization (ATRP) to synthesize silica colloids with SP/methyl methacrylate (MMA) polymer shell
- New particles characterized by much higher loading of SP molecules and enhanced stability.



TEM pictures of 284 nm silica particles with 20 nm SP/MMA polymer coating containing 20 mol % of SP molecules

ATRP Reaction Kinetics for SP/MMA Colloids

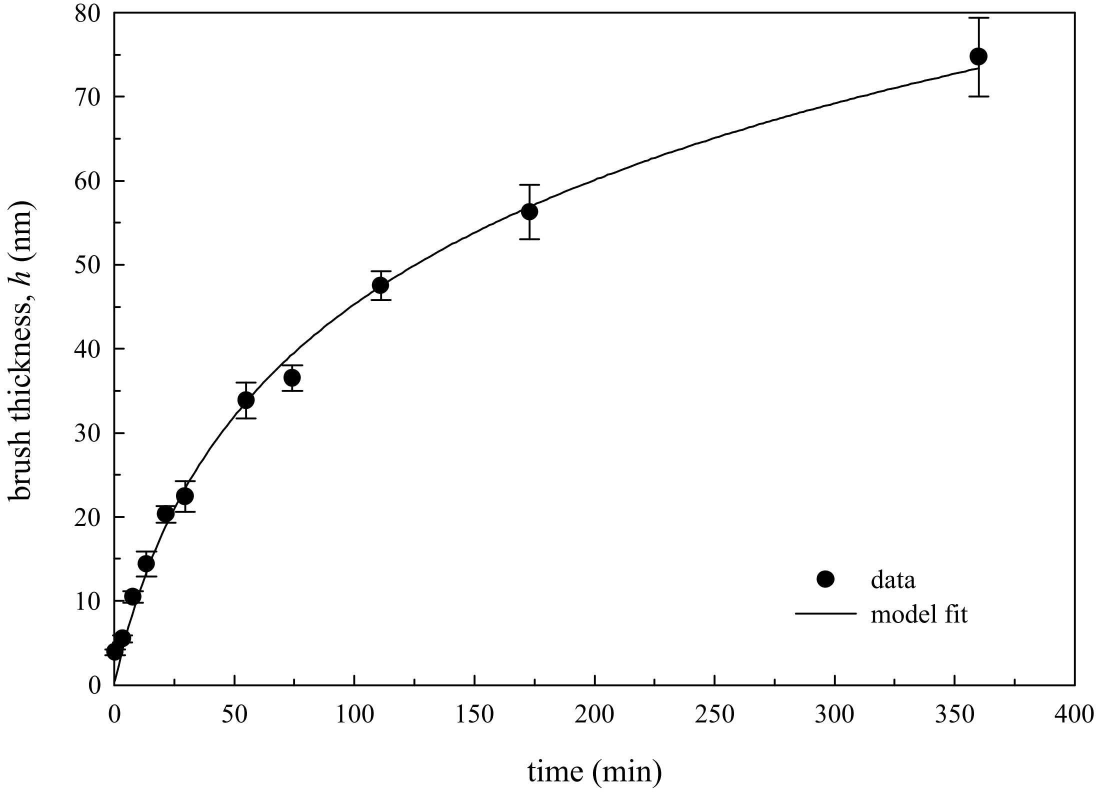
Model

$$\frac{d[A]}{dt} = -k_1[A]^2$$

$$\frac{dh}{dt} = k_2[A]$$

$$h = (k_2/k_1)\ln(1 + k_1[A]_0 t)$$

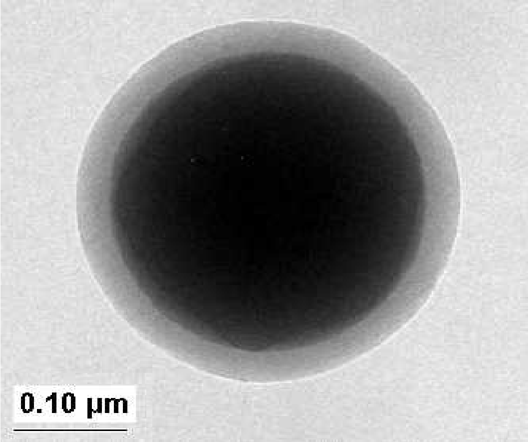
- Fit to the model of Kim *et al.*† indicates the presence of termination reactions



† J. –B. Kim, W. Huang, M. L. Bruening, G. L. Baker, "Synthesis of Triblock Copolymer Brushes by Surface-Initiated Atom Transfer Radical Polymerization," *Macromolecules* **35** (2002) 5410-5416.

Synthesis of SiO_2 SP-MMA Core-Shell Particles

- Polymer shells up to ~80 nm thick
- Control over thickness by adjusting monomer concentration or reaction time
- Control over shell composition by adjusting SP/MMA monomer ratio
- Possibility of re-growth from already polymerized shell using the same or different polymer (under investigation)



284 nm silica spheres with 30 nm thick SP/MMA shells (composition: 22% SP / 78% MMA by NMR)

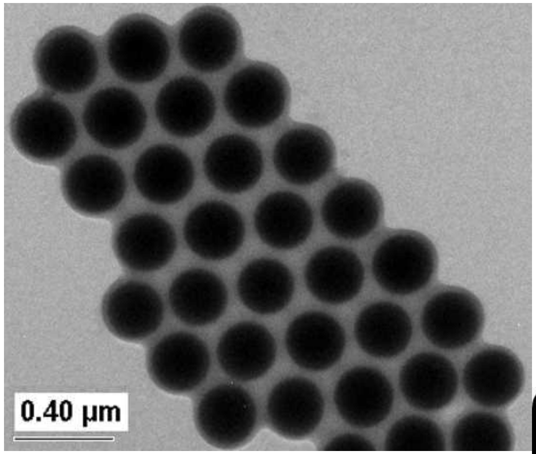
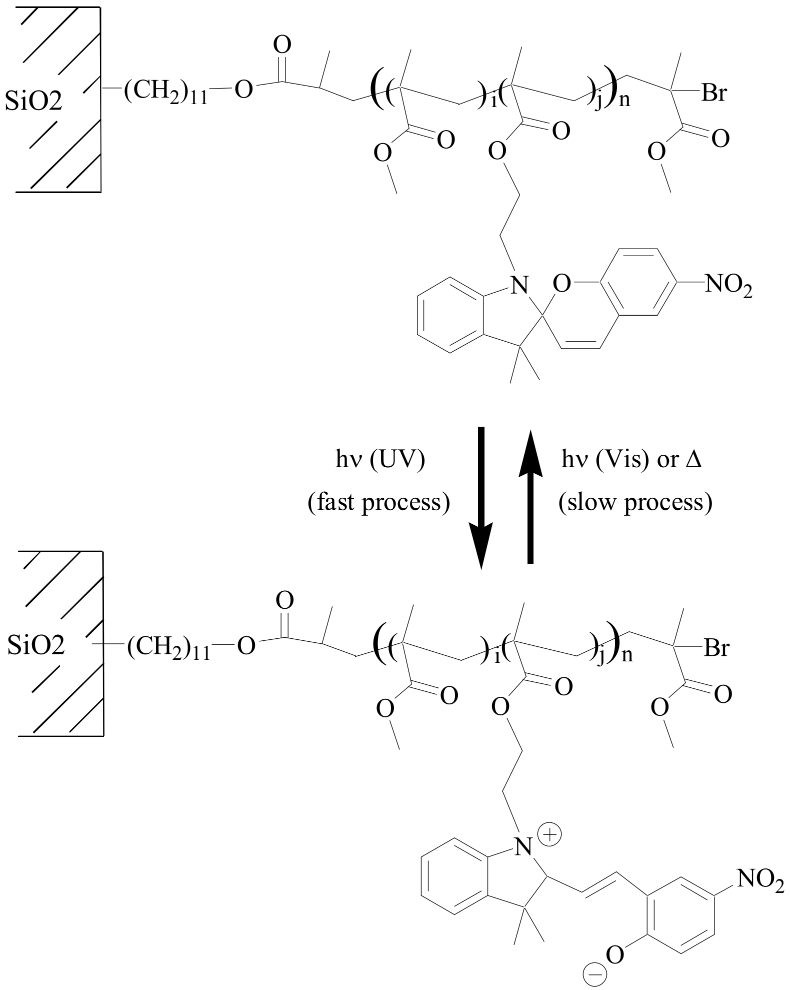


Photo-induced switching



- In non-polar solvents spyrobenzopyran (SP) molecule exists in closed form
- UV excitation causes ring-opening photoisomerization
- After UV treatment molecule exists in zwitterionic merocyanine (ME) form
- Corresponding polarity change alters polymer conformation and polymer-solvent interactions
- Process is reversible (albeit slower) upon exposure to visible light or heat

Photoaggregation of SP-MMA Particles in Toluene

no UV exposure **after 1 min UV**

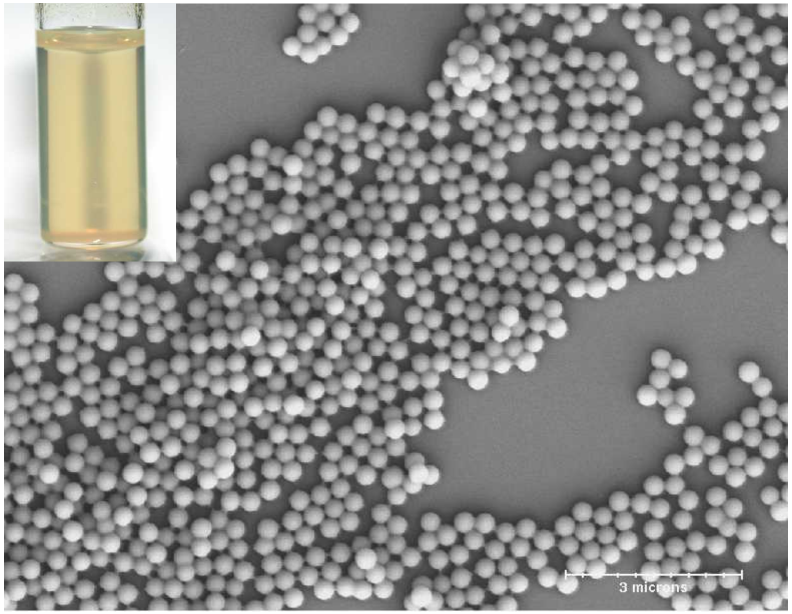
time = 5 sec after shaking **time = 30 sec** **time = 45 sec** **time = 90 sec**

- with SP molecules in non-polar, closed form particles are yellow and well dispersed

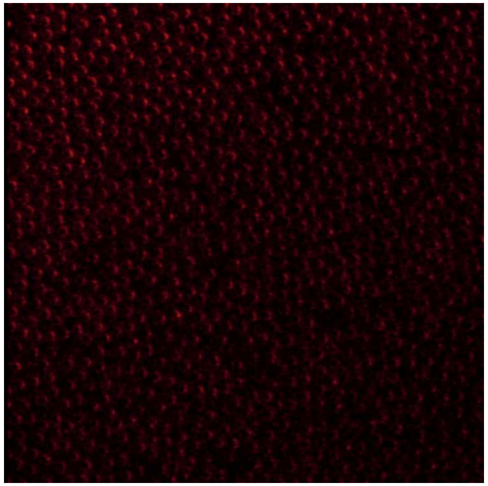
- UV exposure (l=366 nm) induces aggregation with SP molecules now in polar, open form; purple particle aggregates quickly sediment

Sedient Comparison via SEM and Confocal Microscopy

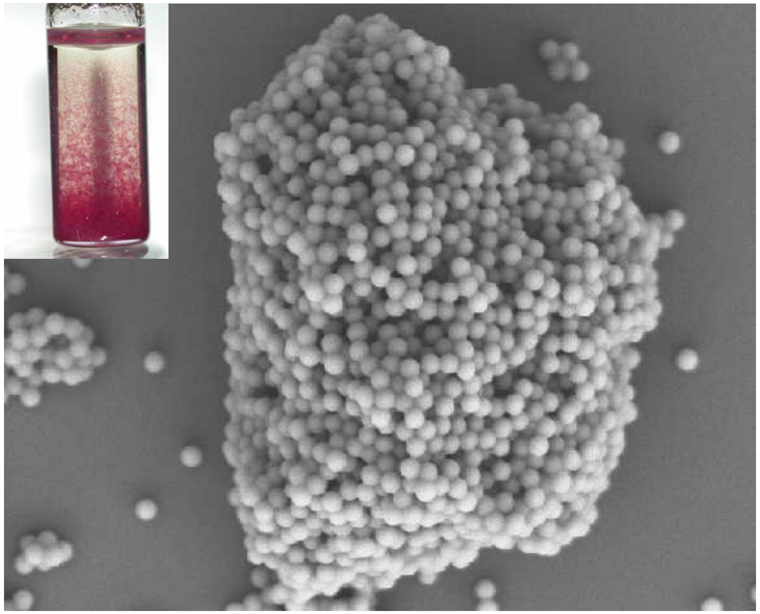
No UV exposure



- particles form well spread mono- and multi-layers
- predominant hexagonally packed domains



After 1 min UV irradiation (l=366 nm)



- larger aggregates present in addition to mono- and multi-layers
- aggregates characterized by random particle packing

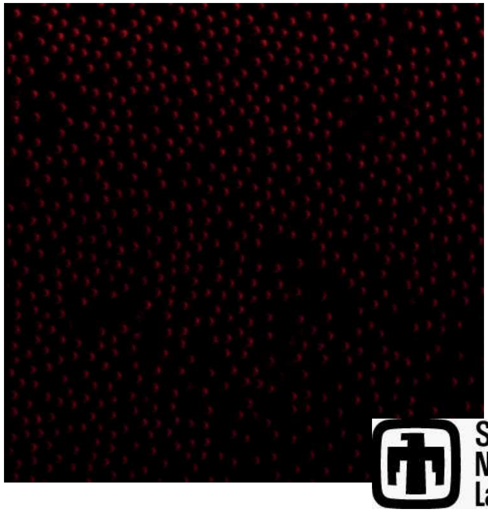
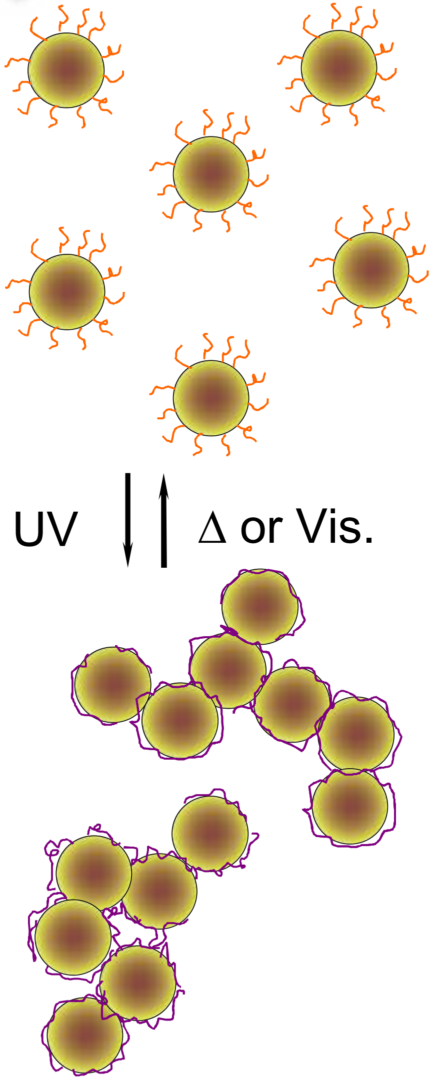


Photo-control of Viscosity in Colloidal Systems



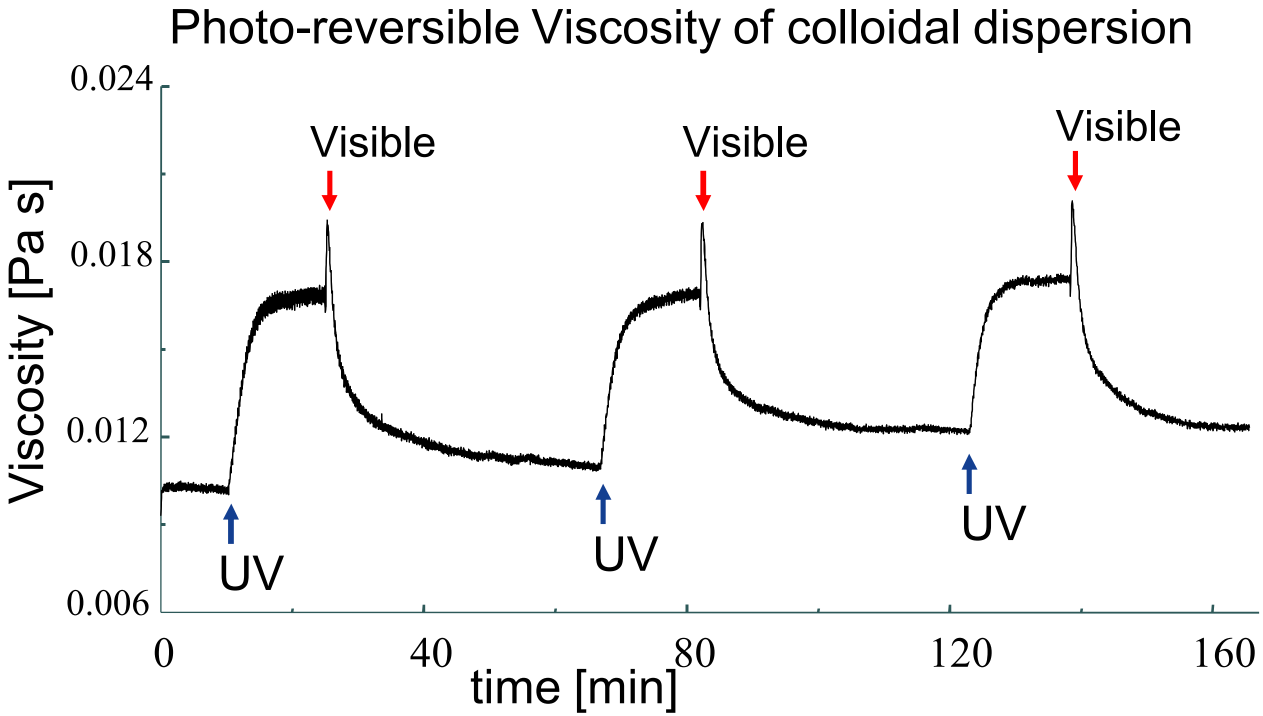


Photo-reversible Viscosity of colloidal dispersion

1 μm SP/MMA modified colloids (20% SP) in toluene at ~30 vol.%

N.S. Bell and M Piech, *Langmuir* **200**6, *22*, 1420-1427.

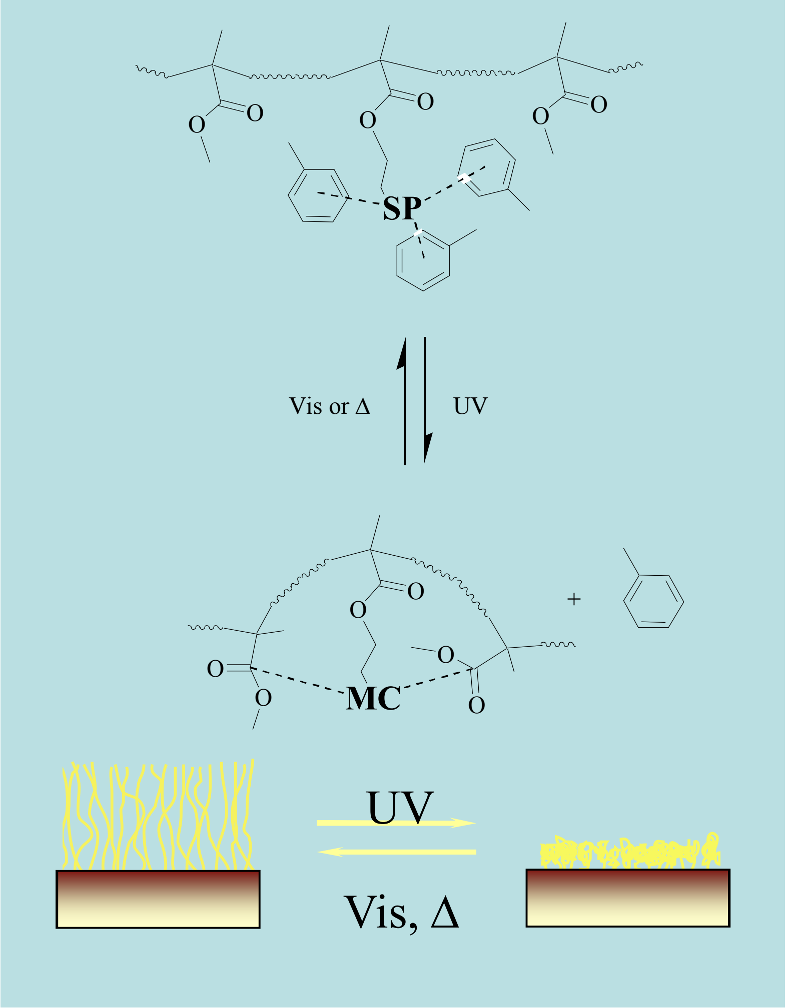
Effects of Photo-Isomerization on SP/MMA Polymers

- Free SP/MMA polymers reduce solution viscosity upon UV irradiation due to polymer chain shrinkage (Irie *et al.*, Golburt *et al.*)

- Chain shrinkage is most pronounced in non-polar solvents (*e.g.*, toluene) and disappears in polar media (*e.g.*, dichloroethane)

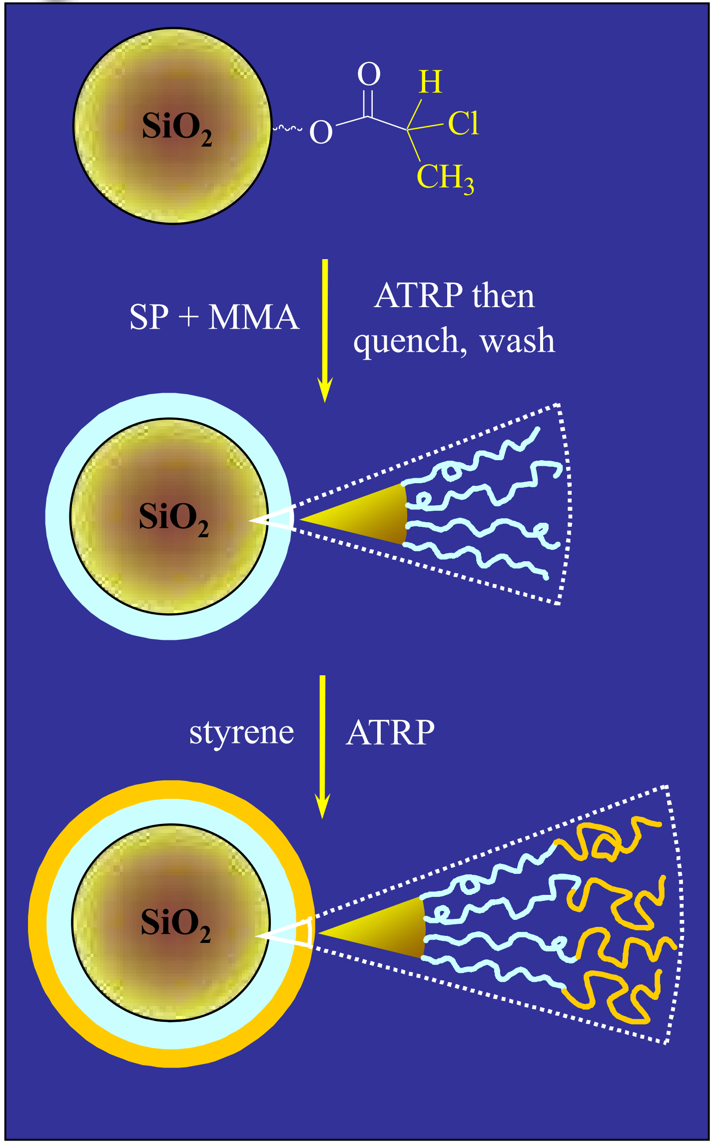
- Process caused by specific intramolecular solvation of polar merocyanine form by MMA ester side groups in competition with solvation by solvent

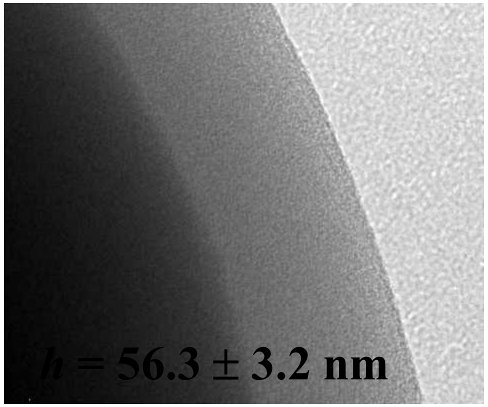
- Polymer shrinkage also demonstrated on flat surfaces by as much as 30 nm for 45 nm thick films in non-polar solvents (Ito, *et al.*)



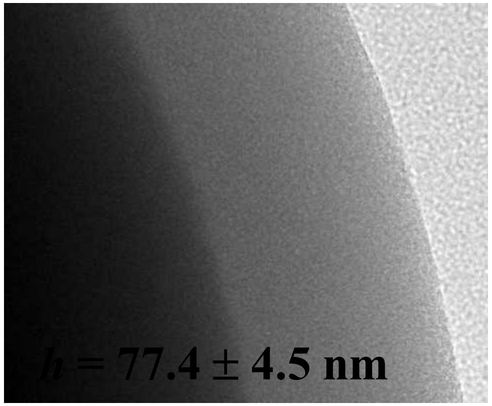
Subsequent Block Co-Polymerization

- SP-MMA layers quenched and reacted with styrene
- confirms ‘living’ character of polymerization
- adds versatility in functional system design





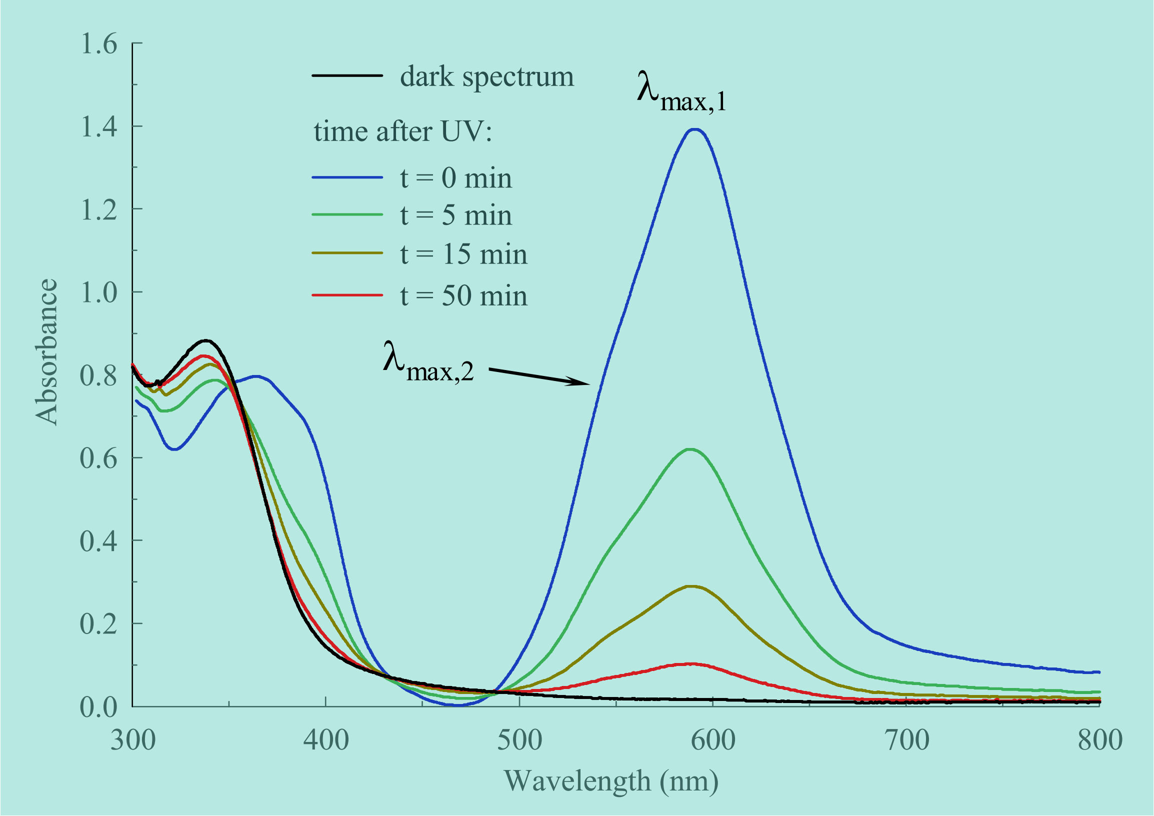
aggregation in toluene post UV treatment



stable in toluene post UV treatment

UV-Vis Characterization

Spectra in Tetrahydrofuran (THF) Solvent

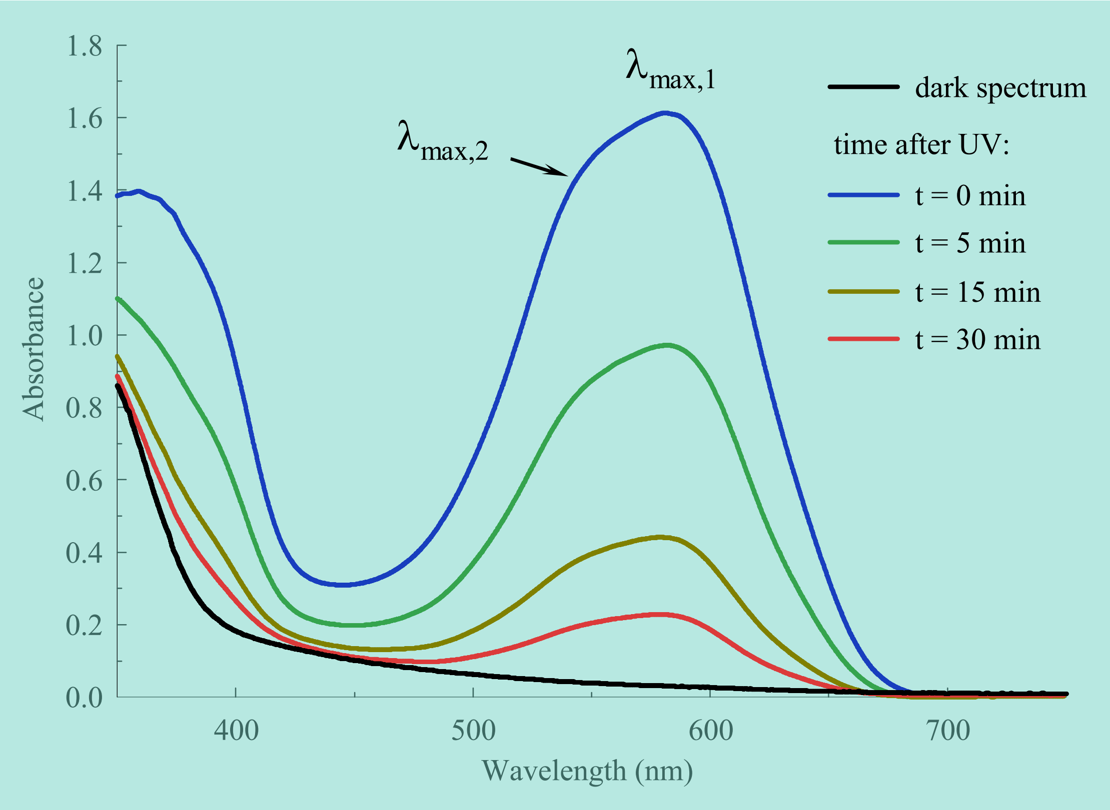


Spectrum of 20% SP / 80% MMA polymer attached to 1 μm SiO_2 colloids at concentration of 0.079% wt/wt in THF

- $\lambda_{max,1}$ = 589 nm due to ME
- $\lambda_{max,2} \approx$ 550 nm due to ME-SP aggregates
- identical spectra obtained for attached and free polymers
- SP monomer shows only $\lambda_{max,1}$ = 587 nm due ME
- SP local environment within SP/MMA polymers favors ME-SP aggregation

UV-Vis Characterization

Spectra in Toluene Solvent

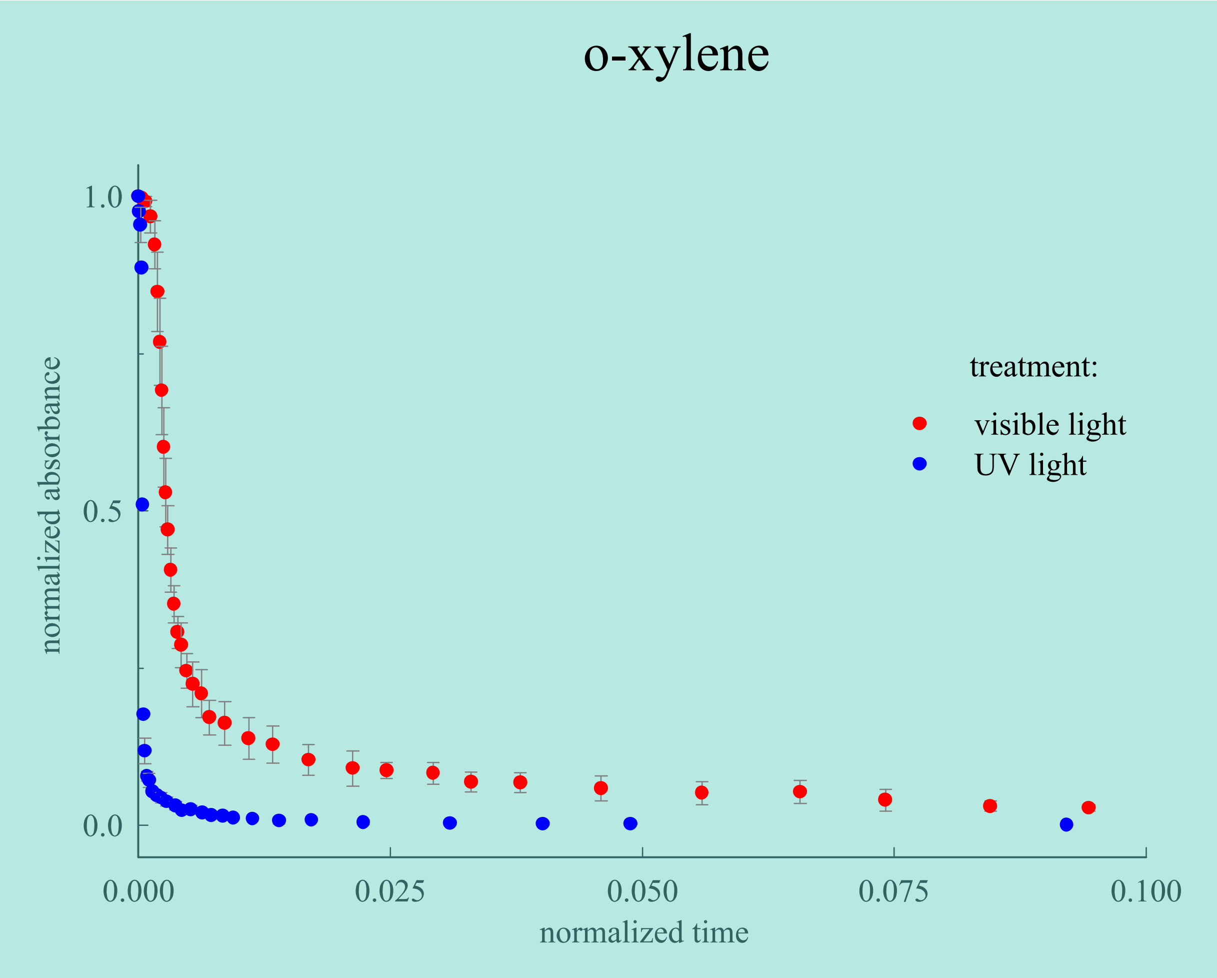


Spectrum of 20% SP / 80% MMA polymer attached to 1 μm SiO_2 colloids at concentration of 0.20% wt/wt in toluene

- $\lambda_{max,1}$ = 581 nm due to ME
- $\lambda_{max,2} \approx$ 545 nm due to ME-SP aggregates
- $\lambda_{max,1}$ diminished relative to $\lambda_{max,2}$ in toluene compared to THF
- This points to better ME solvation by THF vs. toluene
- $\lambda_{max,1}$ and $\lambda_{max,2}$ blue shifted in toluene compared to THF
- This points to more polar ME micro-environment in toluene vs. THF

Sandia National Laboratories

Sedimentation in different solvents

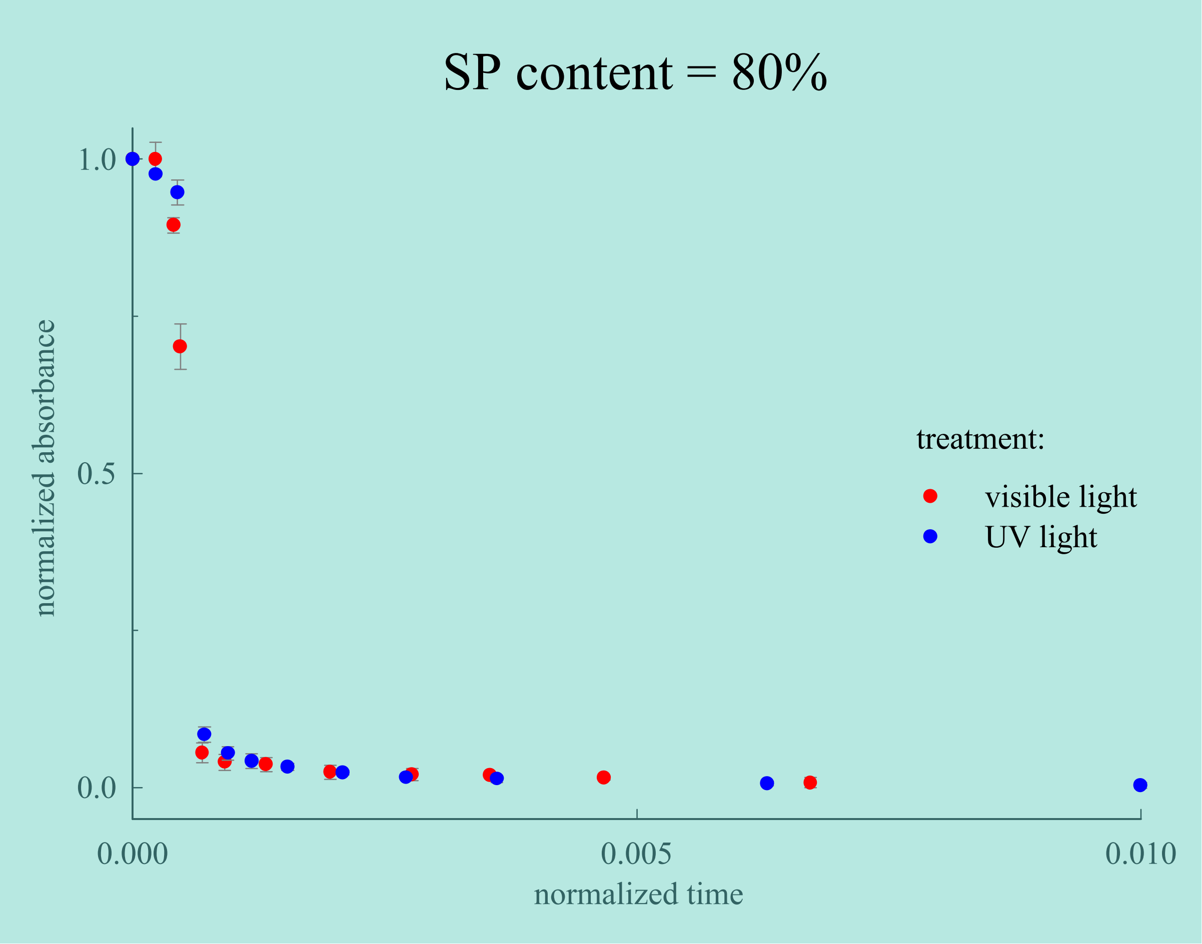


- Surface Layers contain 20 mol% spirobenzopyran molecules in PMMA shell.
- Time axis normalized by theoretical sedimentation time (Stokes equation)

$$t = \frac{18\eta_L H}{a^2\left(D_p - D_L\right)g}$$

- Decrease in solvent polarity causes stronger aggregation
- UV irradiation precipitates stronger aggregation in in border-line solvents

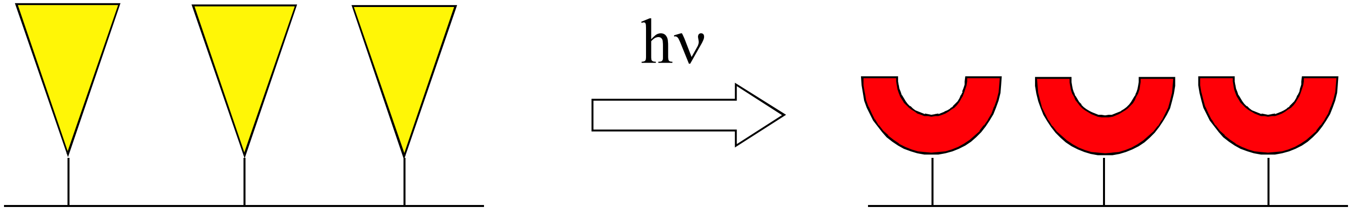
Sedimentation with different spiropyran content particles



- Sedimentation studied in toluene solvent for each SP concentration
- Increase in SP content causes stronger aggregation
- UV irradiation precipitates stronger aggregation in in border-line solvents
- Photo-aggregation is sensitive to solvent and %SP; polymer solubility factors can be adjusted for different systems.

Photochemical Control of Surface Interactions

Photochemical alteration of an organic moiety resulting in a change in steric, electrostatic parameters



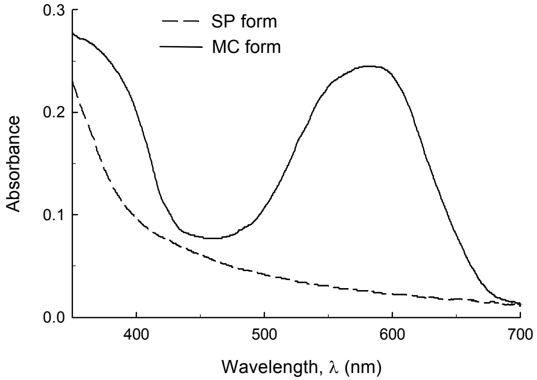
- Real-time manipulation of surface properties
- Switchable/reversible (new operational modes)
- Non-invasive/remote control over stability

time = 5 sec after shaking

time = 90 sec

Manifested in:

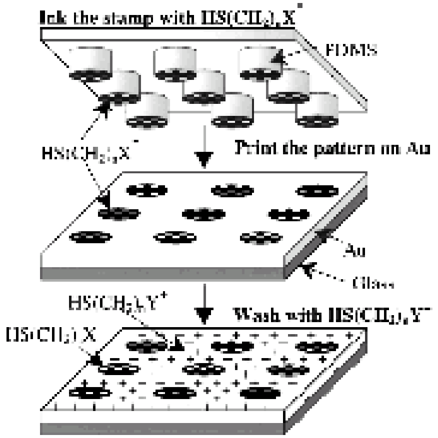
- changes in optical profile (UV/Vis spectrum)
- alteration of surface energy
- photocontrolled colloidal stability

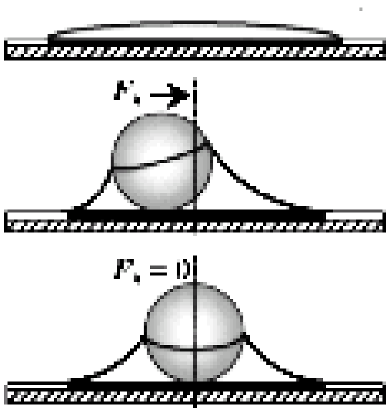


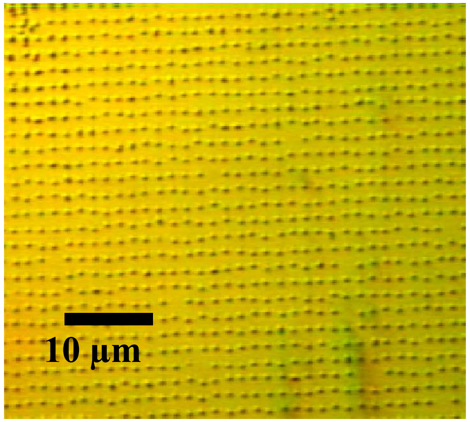
Surface Templating of Particle Assembly

Cationic/anionic functionalization of particles and substrates enables
-single particle spectroscopy
-definition of ABAB composite architectures for energy transfer

Particle templating
via microcontact
printing (mCP)
of heterogeneous
monolayers:





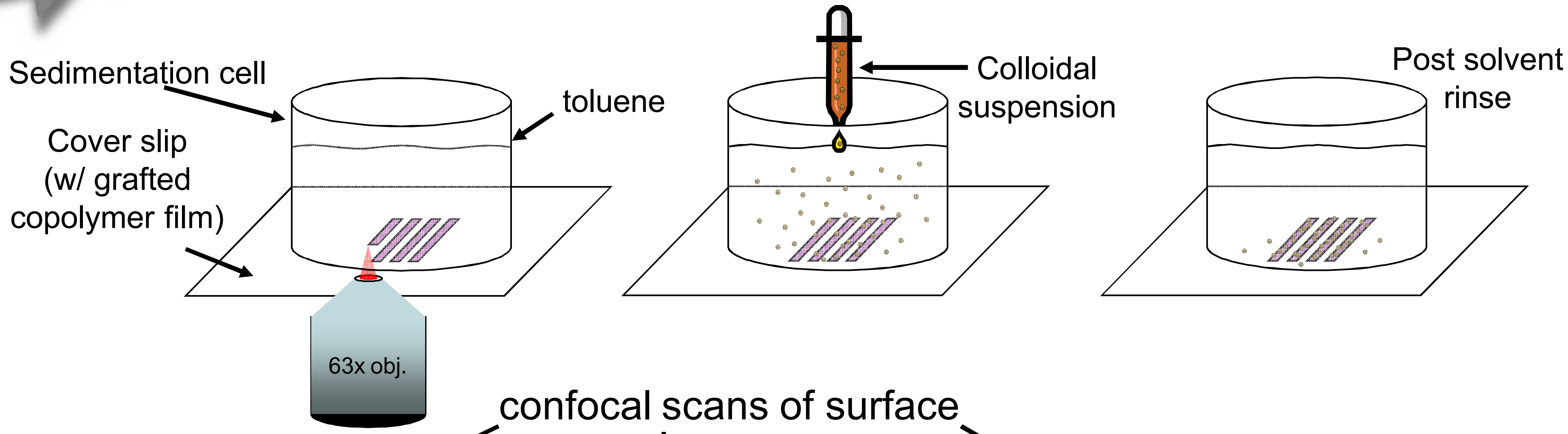


Particle templating allows:

- more complicated structures: FCC, BCC, diamond cubic
- introduction of defects (superlattices)
- stamping of waveguides

Clem and Payne, "Monolayer-mediated patterning of electroceramics," J. Electroceram, 3(2), 163 (1999).
Aizenberg, Braun, and Wiltzius, "Patterned colloidal deposition by electrostatic and capillary forces, Phys. Rev. Lett. **84**(13), 29973000 (2000).

2D Photo-defined Colloidal Adsorption



Sedimentation cell

Cover slip (w/ grafted copolymer film)

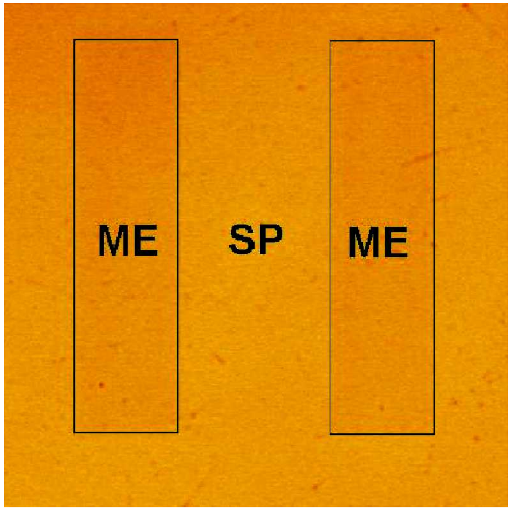
toluene

63x obj.

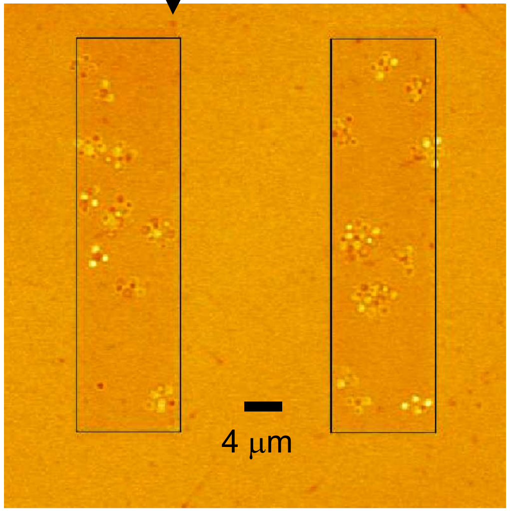
Colloidal suspension

Post solvent rinse

confocal scans of surface

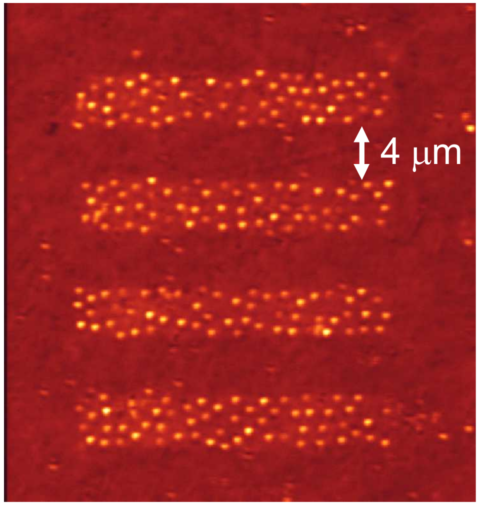


exp. start, t = 0



clusters, t = 660 s

2D patterning example



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

Photo-Actuated Deposition in Toluene

SPMMA-*co*-MMA coated glass slide in toluene

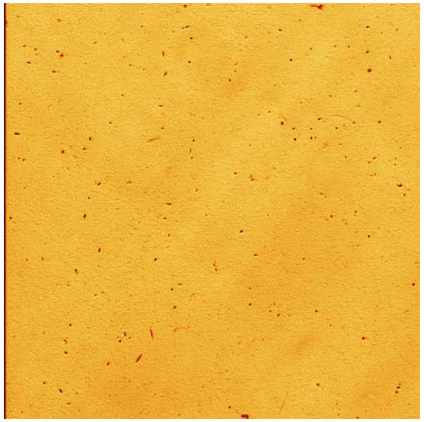
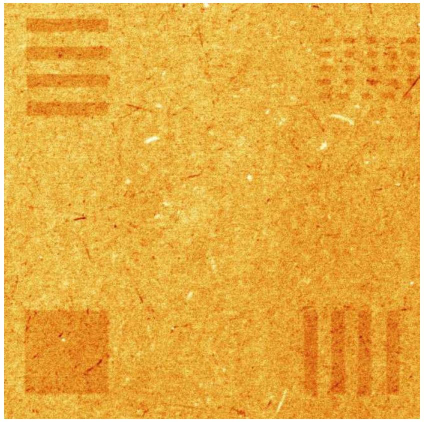
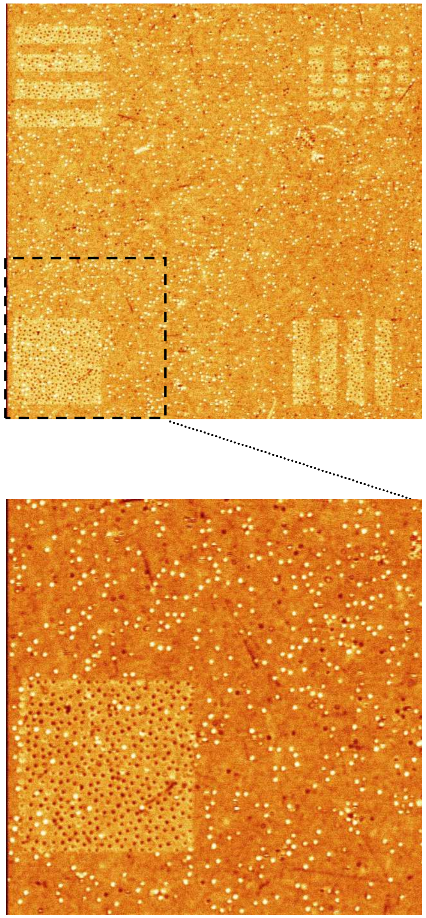


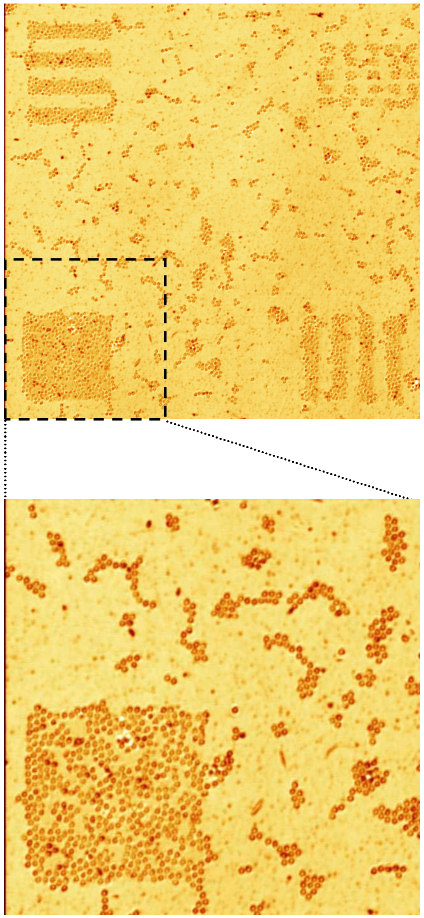
Photo-isomerizing SP in dark regions



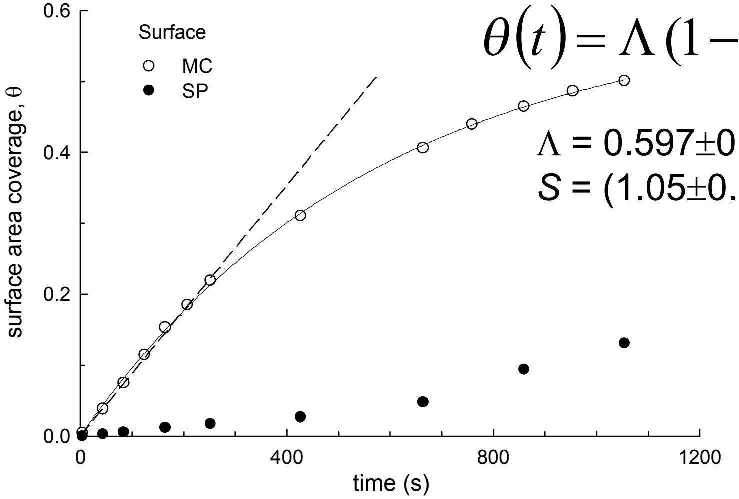
After settling dilute colloidal suspension



After drying



particle adsorption kinetics

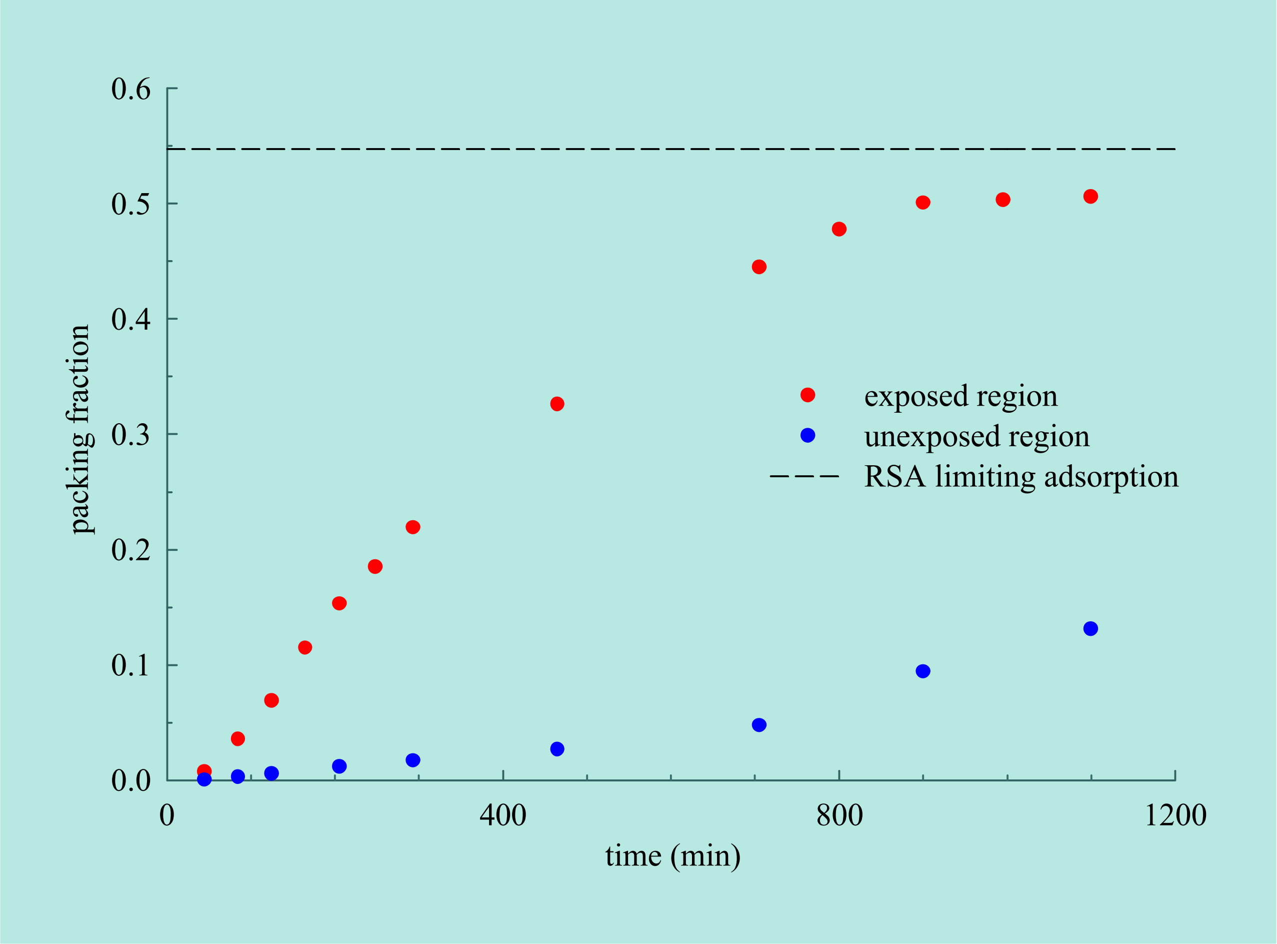


$$\theta(t) = \Lambda\,(1 - e^{-S\,t/\Lambda})$$

$\Lambda = 0.597 \pm 0.007$,
$S = (1.05 \pm 0.02) \times 10^{-3}\ \mathrm{s}^{-1}$

The deposition behavior falls between random sequential adsorption and ballistic deposition models, with a time constant near the sedimentation rate.

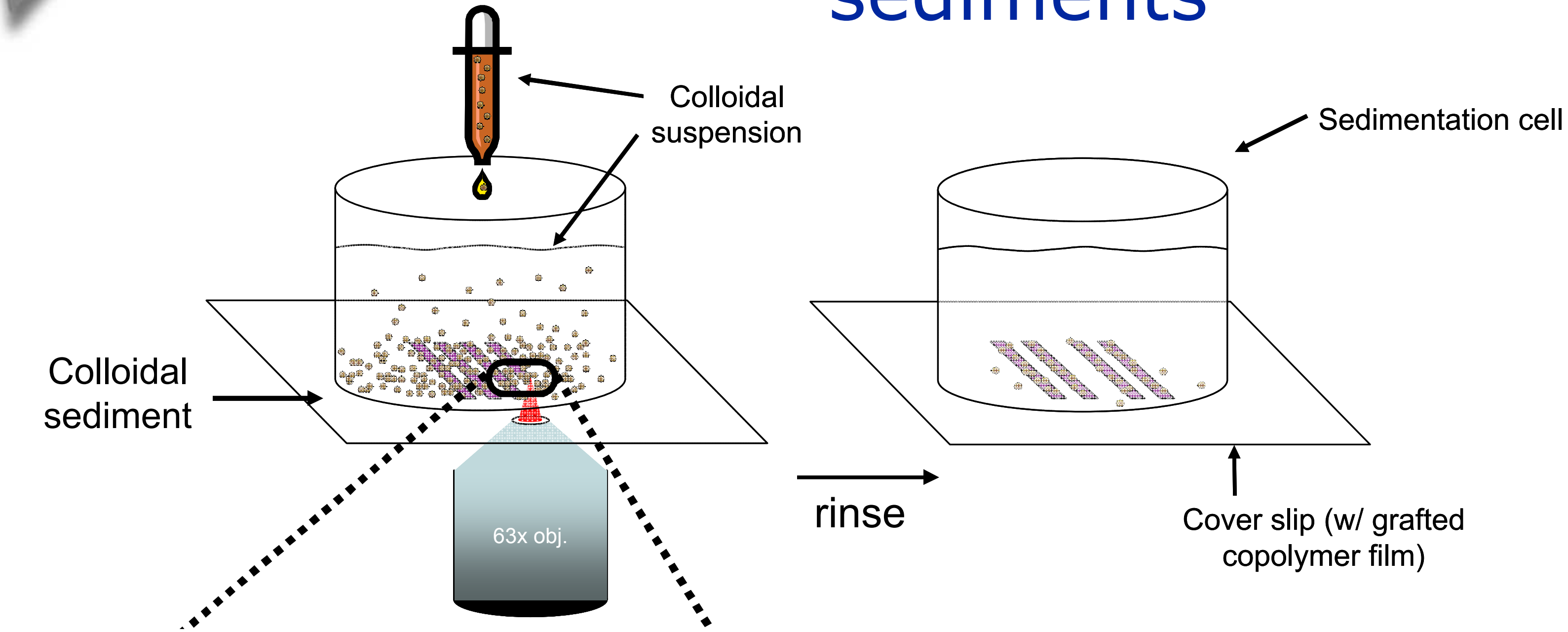
Kinetics of photo-actuated deposition



- Initially particles adsorb 14× more selectively to the exposed regions containing ME

- Following rinsing and drying particle density is 10× higher in exposed regions

3D laser gel-writing in colloidal sediments

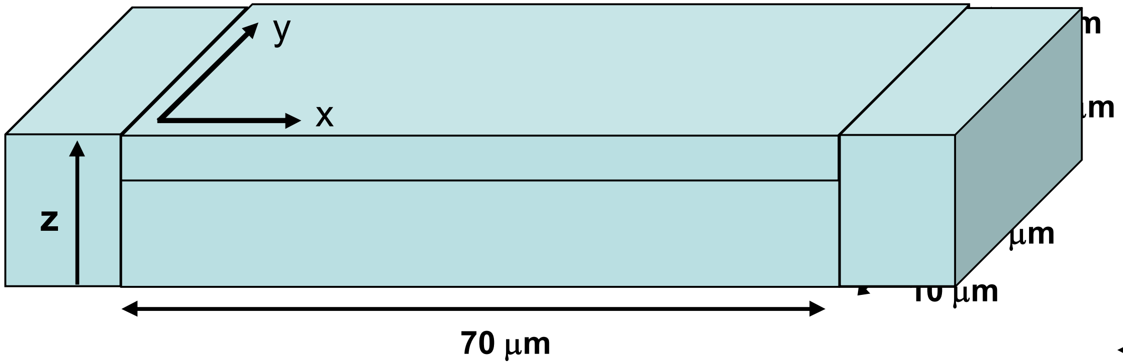


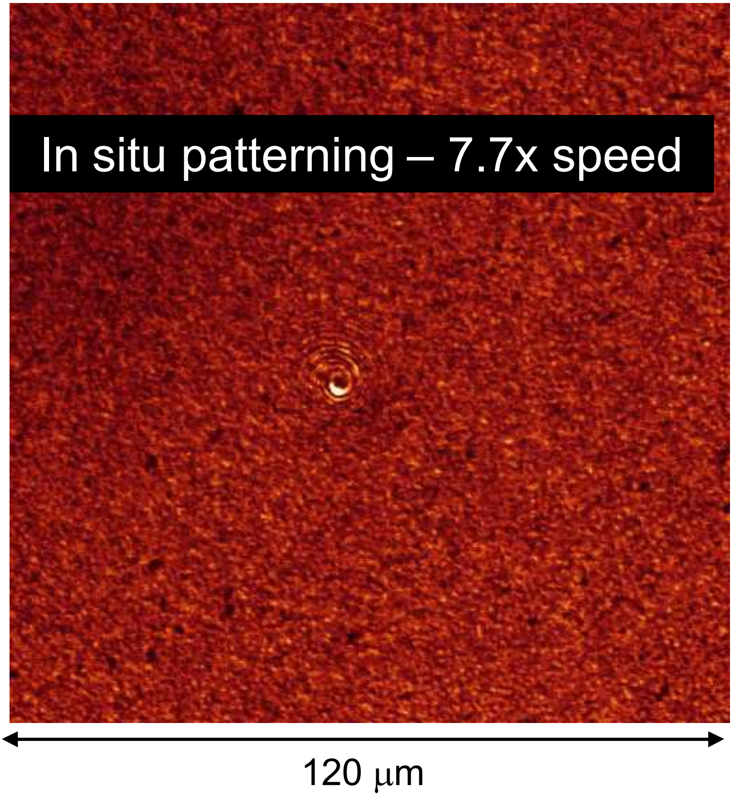
M.C. George et al., *Adv. Mater.* **2008**, *20*, 1-5.

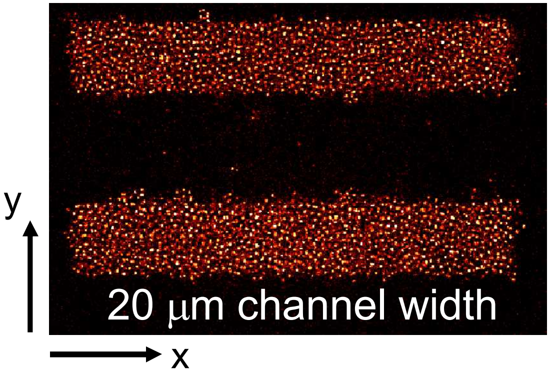
Photo-Patterned Colloidal Gel Micro-channels

Processing Steps

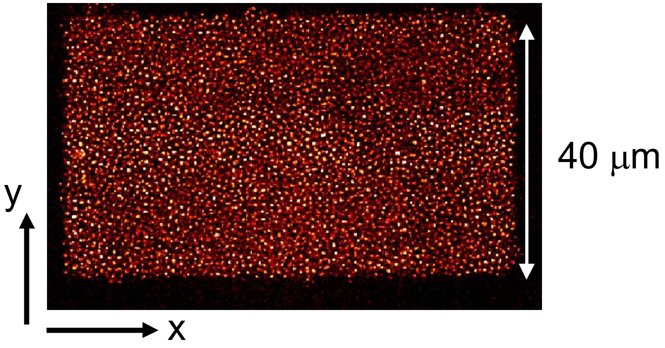
- Introduce colloids, form sediment
- Write walls (via 2PA)
- Write channel top
- Rinse out un-gelled colloids

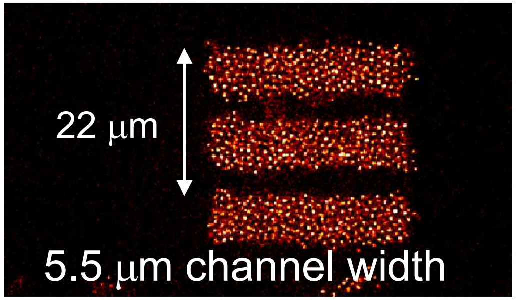



In situ patterning – 7.7x speed



20 µm channel width



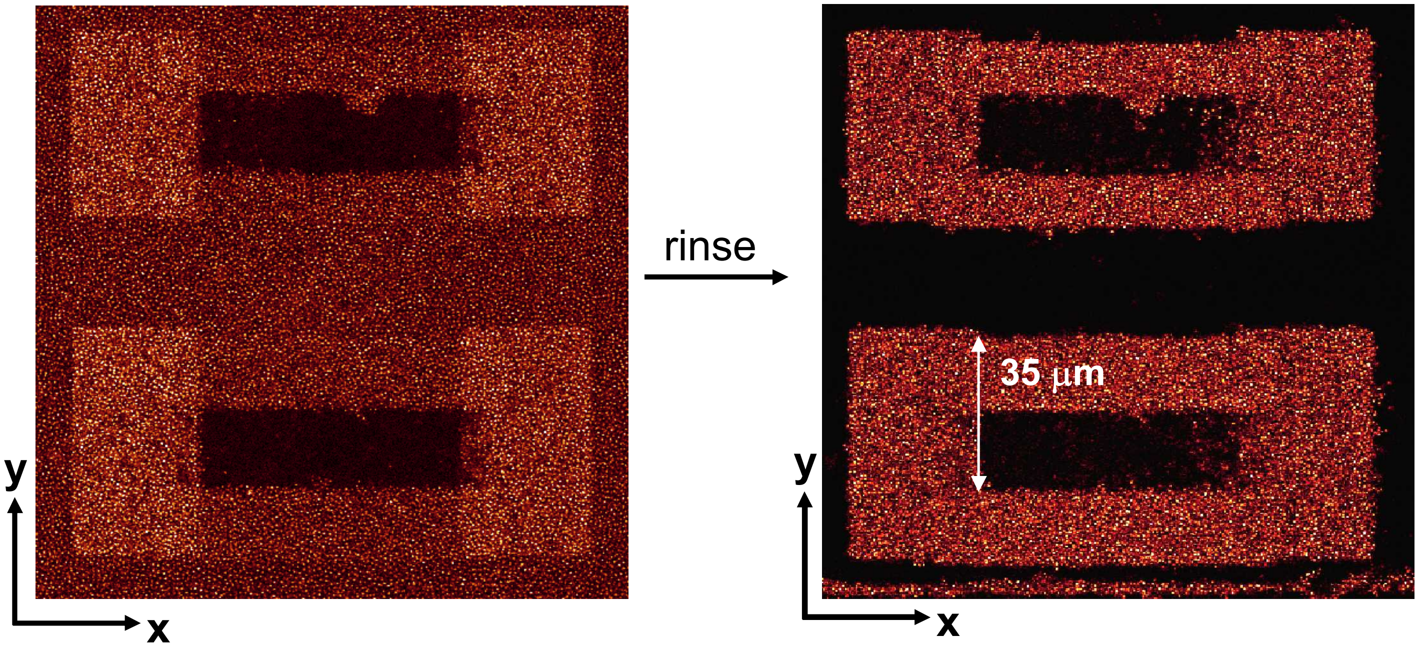


5.5 µm channel width

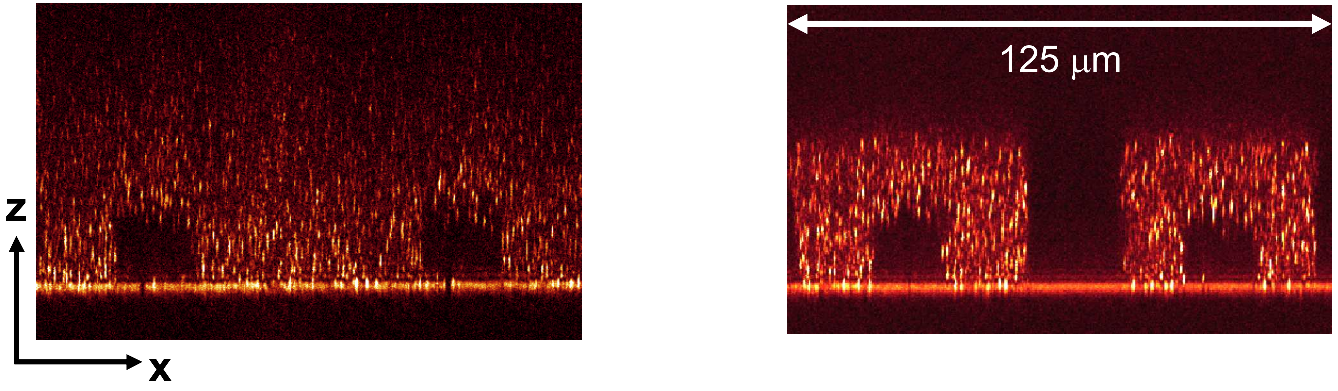
M.C. George et al., *Adv. Mater.* **2008**, *20*, 1-5.

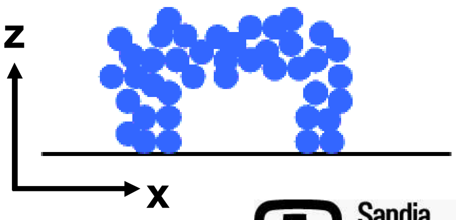
Photo-Patterned Colloidal Gel Micro-cavity

confocal xy reflectance sections



confocal reflectance cross-sections (xz)

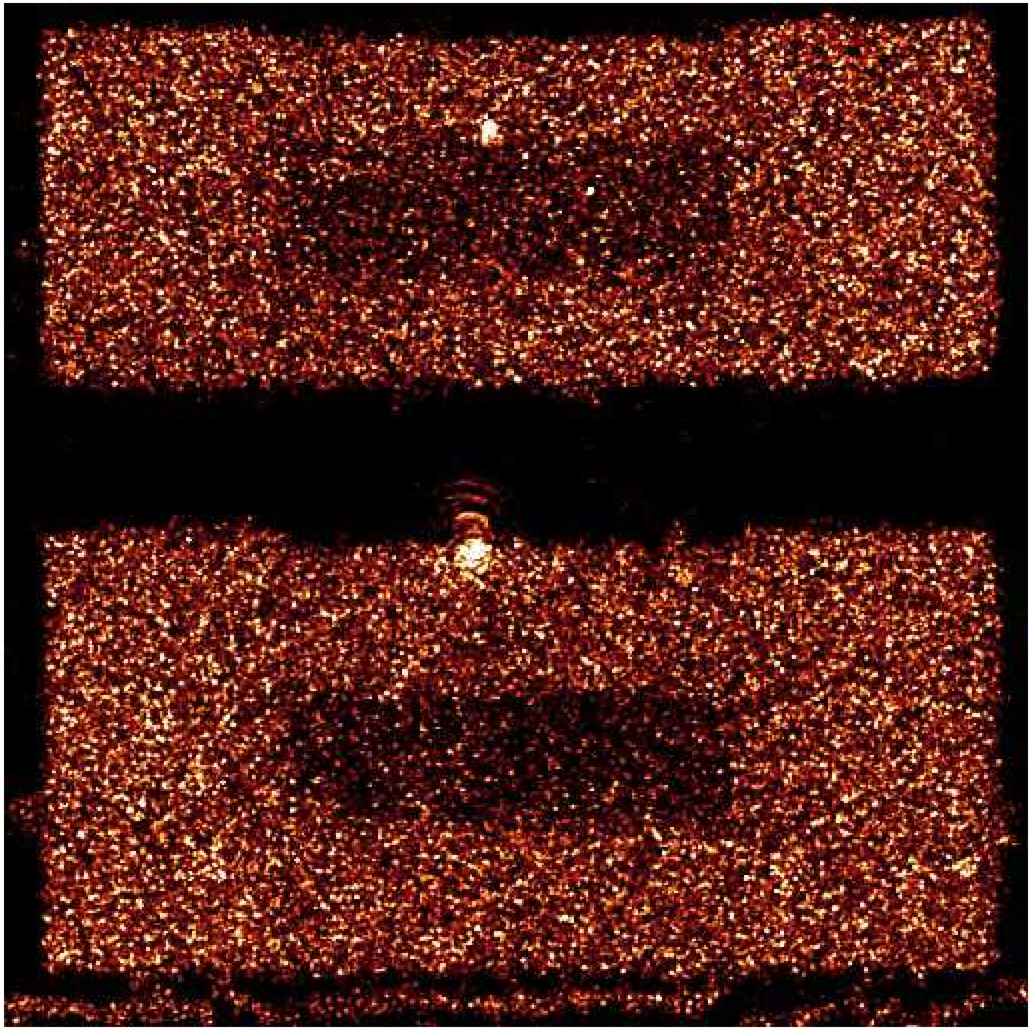




Trapped Colloidal Particles

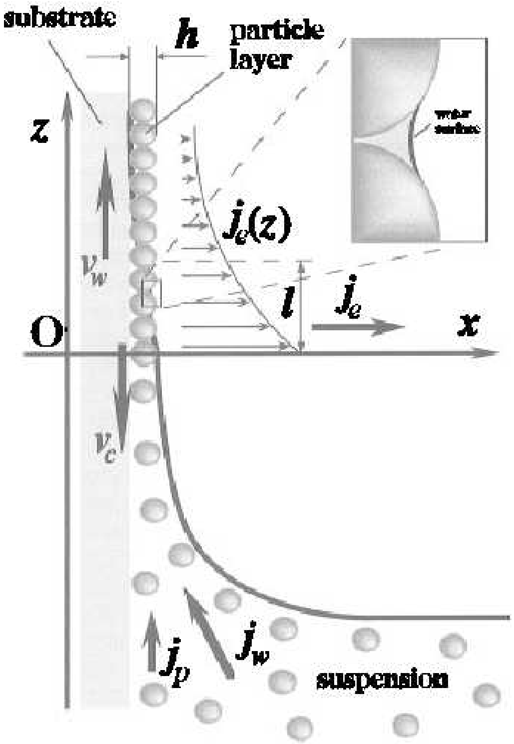
Processing Steps

- form a colloidal sediment
- Write walls (via 2PA)
- Write channel top
- Rinse out un-gelled colloids
- Observe Brownian motion of contained colloids

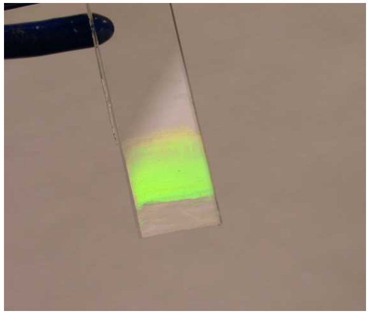


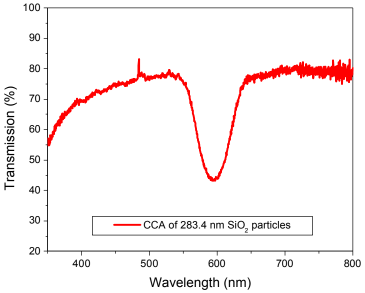
Self Assembly forms Lowest Energy Ordered Structures

A higher level of particle control is required than that of bulk patterning for ordered structures to be fabricated.

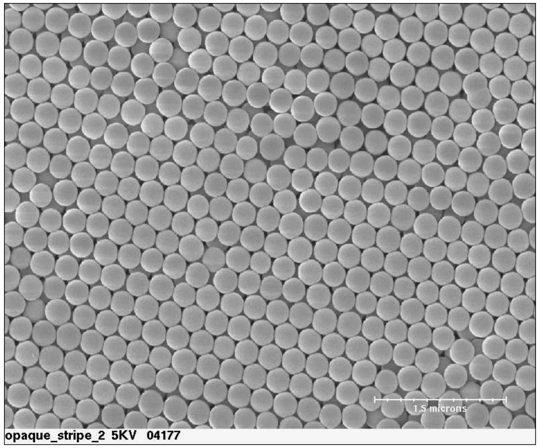


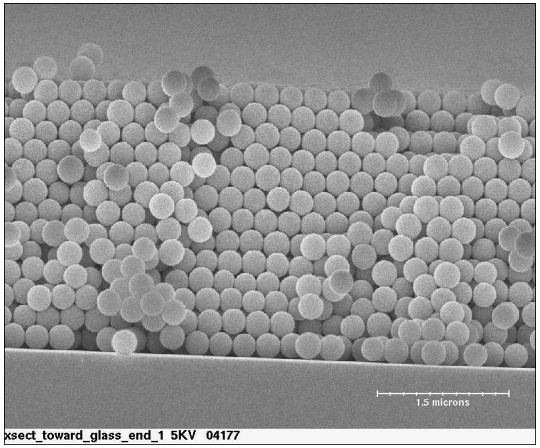
Antony S. Dimitrov † and Kuniaki Nagayama
Langmuir **1996,** *12,* 1303-1311





<u>Forces causing CCA assembly</u>
Capillary forces dominate the arrangement of particles to form ordered arrays. The development of a viscous film (drying, soaps) between particles constrains their arrangement.





Experimental Setup

- A.A Opto Electronic DTSXY-400-1064
- Agilent E3640A DC Power Supply

Laser

- Ventus Doubled YAG (1064nm)
- < 100 mJ, 10 Hz

CMOS

- Vision Research Miro 4, 12 bit
- Up to 100,000 fps

Microscope

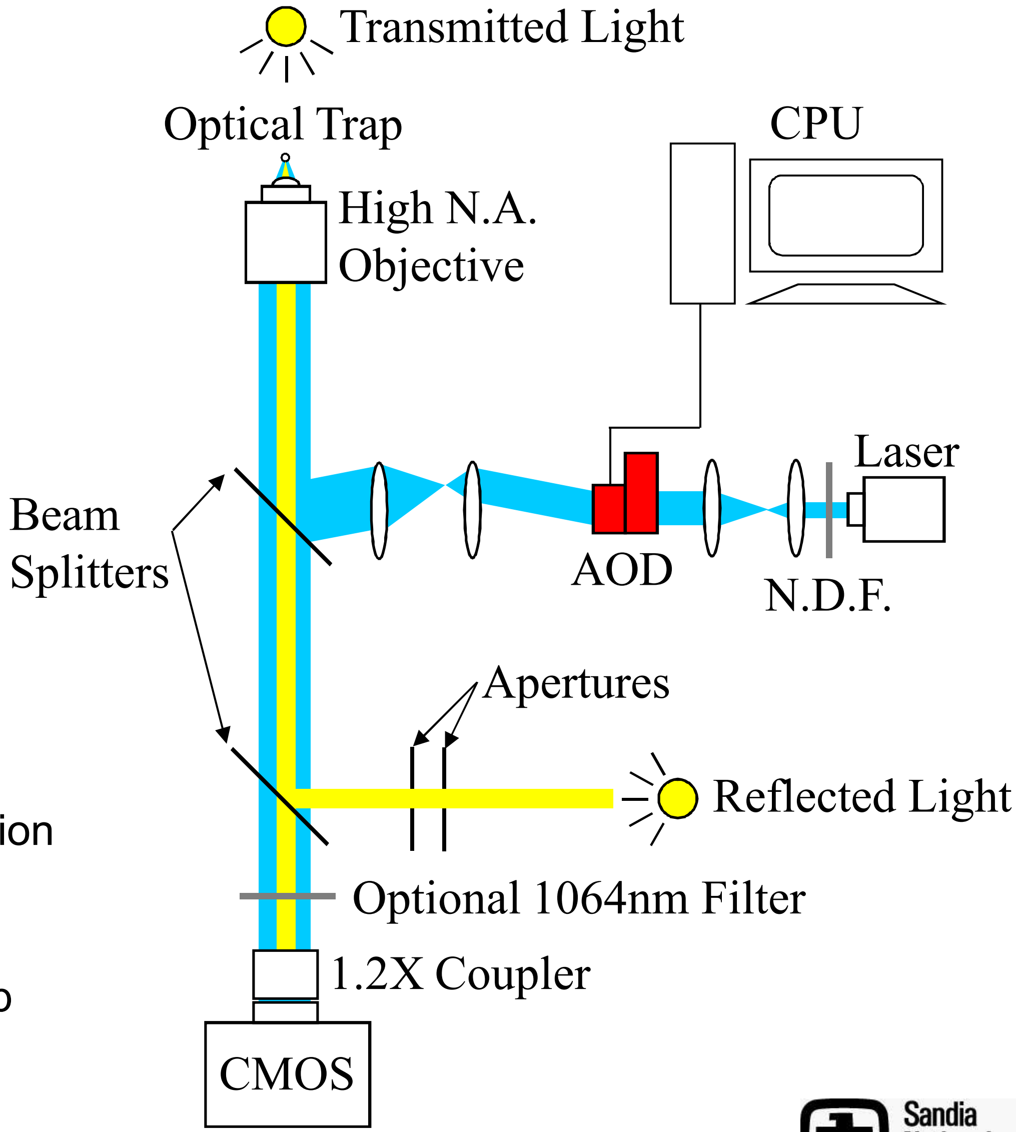
- Nikon TE2000-S
- Prior ProScan II Motorized Stage

High N/A Objective

- Nikon Plan Fluor 100x/1.3 Oil Immersion

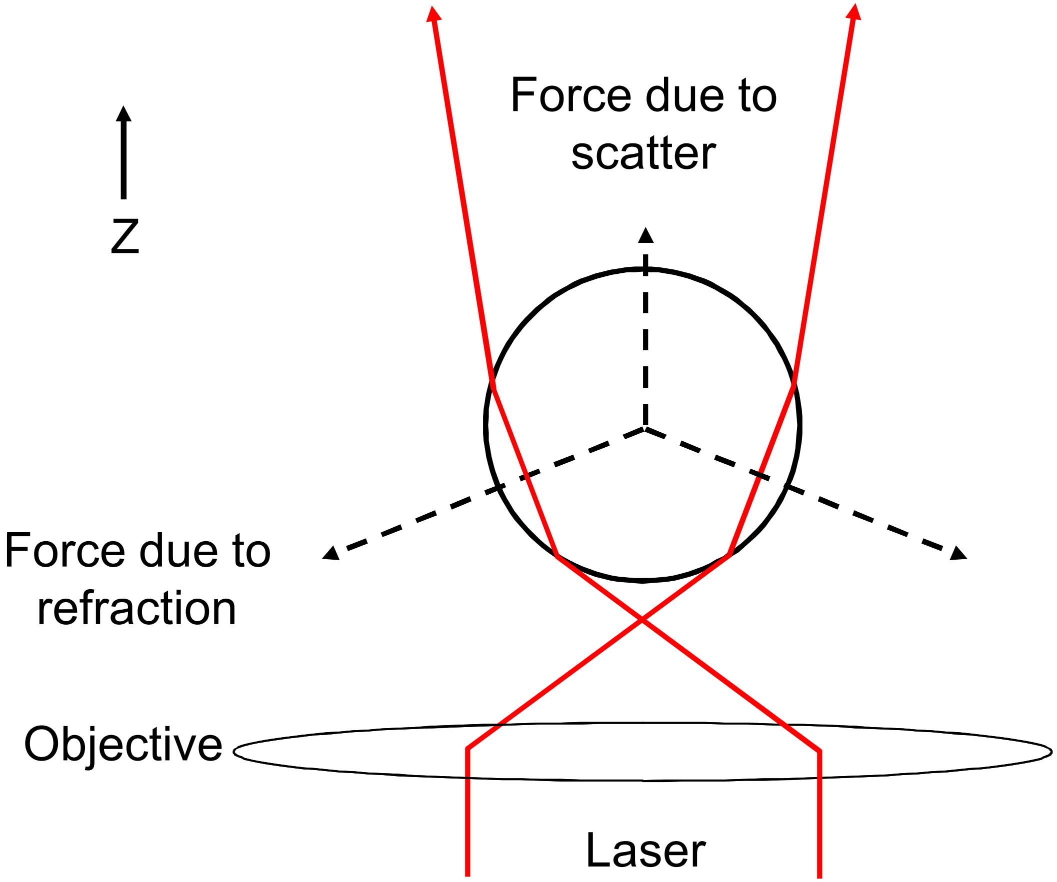
Reflected Light

- EXFO X-Cite Series 120 Hg-Arc Lamp (120W)



A. Grillet et al. Sandia National Laboratory

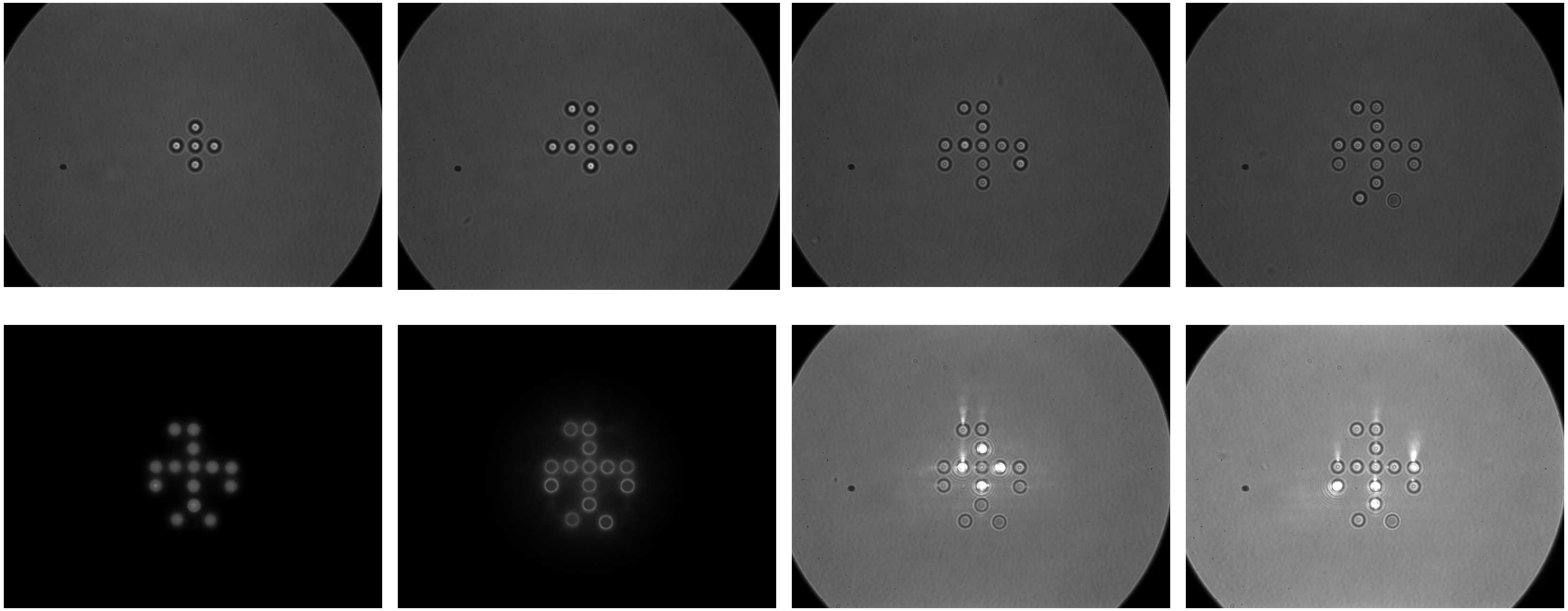
Optical Trapping



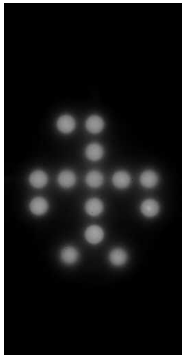
A. Ashkin, J.M. Dziedzic, J. E. Bjorkholm, and Sheven Chu, Observartion of a single-beam gradient force optical trap for dielectric particles, Optics Letters 1989, 5, 288-290.

- Trapping occurs when the force associated from the momentum change of the refracted light balances the force due to light scattering off the surface of the particle.
- The refractive index of the solution must be lower than that of the particle in order for a component of the force due to refraction to be in the negative z direction.
- As the difference between the solvent and particle refractive index increases, the trap stiffness increases (easier to trap particles).

Multiple Optical Traps Allow for Precise Orientation of Silica Particles

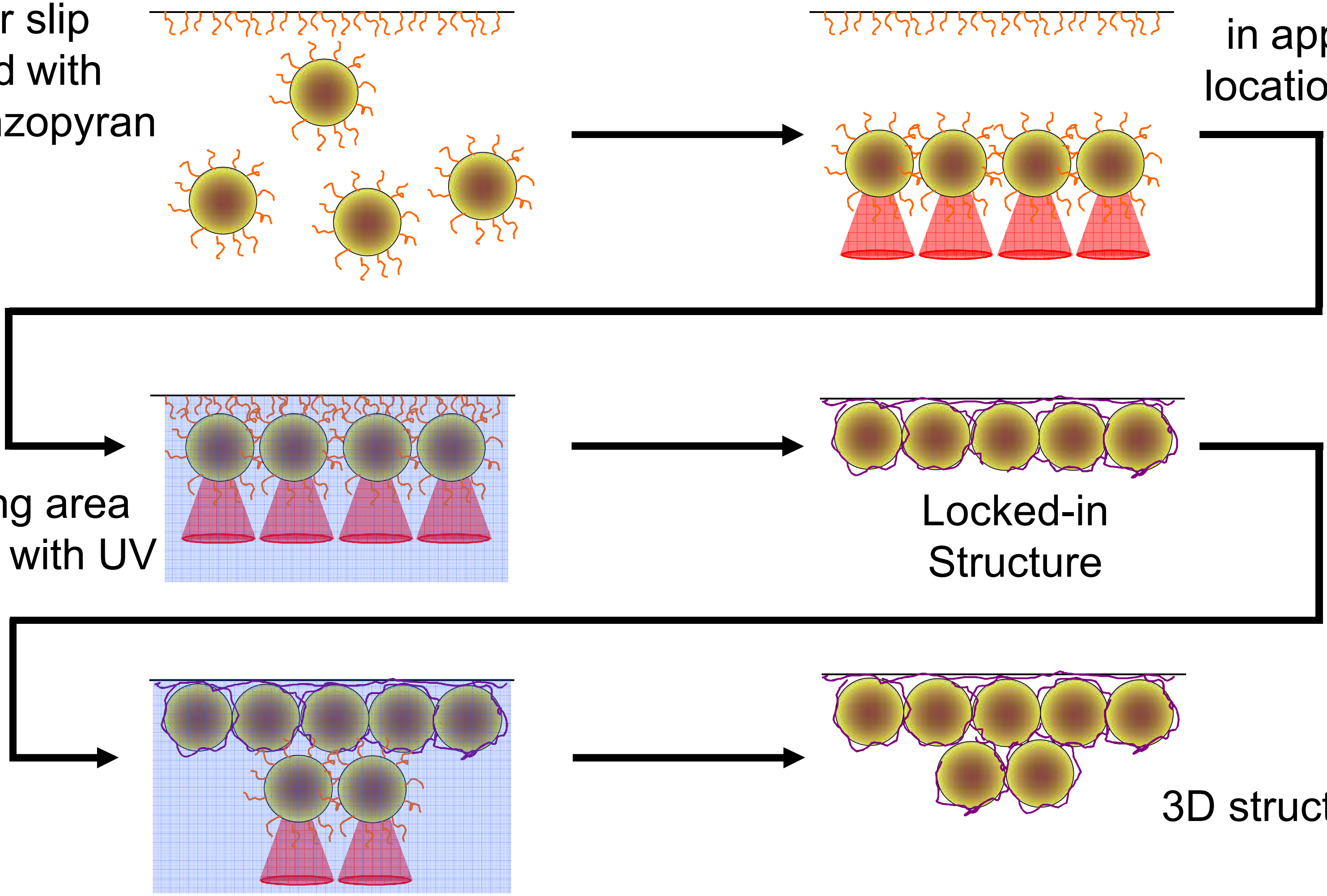


- This structure is built using 14 optical traps.
- These particles are silica (n = x?) in water (?)
- Particles are “caught” by Brownian diffusion into the field of view, and maintained in the position desired by the optical trap.



T. Koehler, et al. unpublished, Sandia National Labs

Route to Structure Fabrication using SP-MMA Functionalized Particles



Cover slip
coated with
Spirobenzopyran

Particles placed
in appropriate
location with OT

Viewing area
flooded with UV

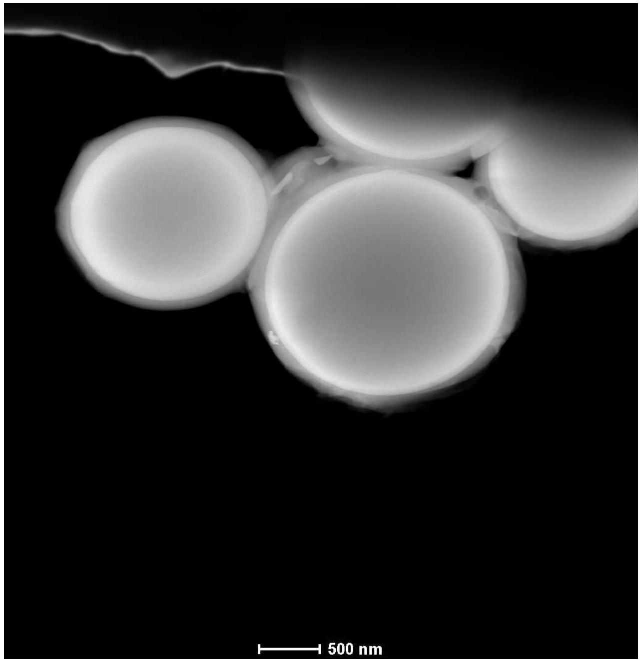
Locked-in
Structure

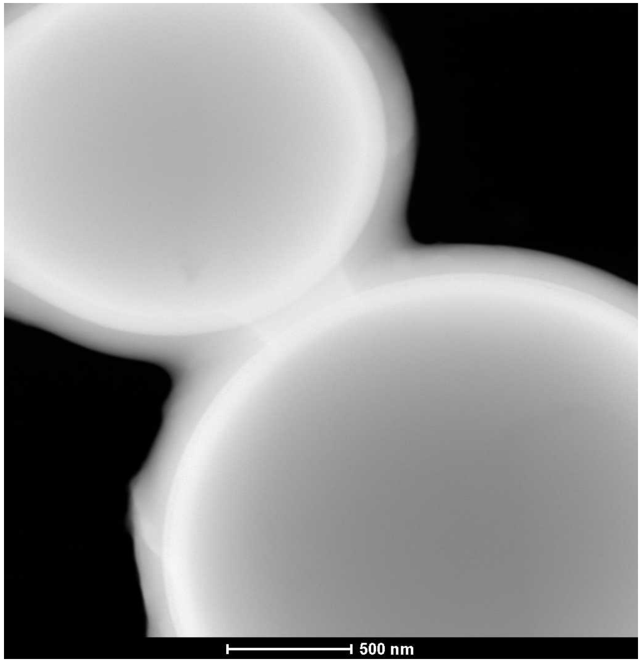
3D structure

Process repeated by grabbing particles that are outside the viewing area (no previous UV exposure)

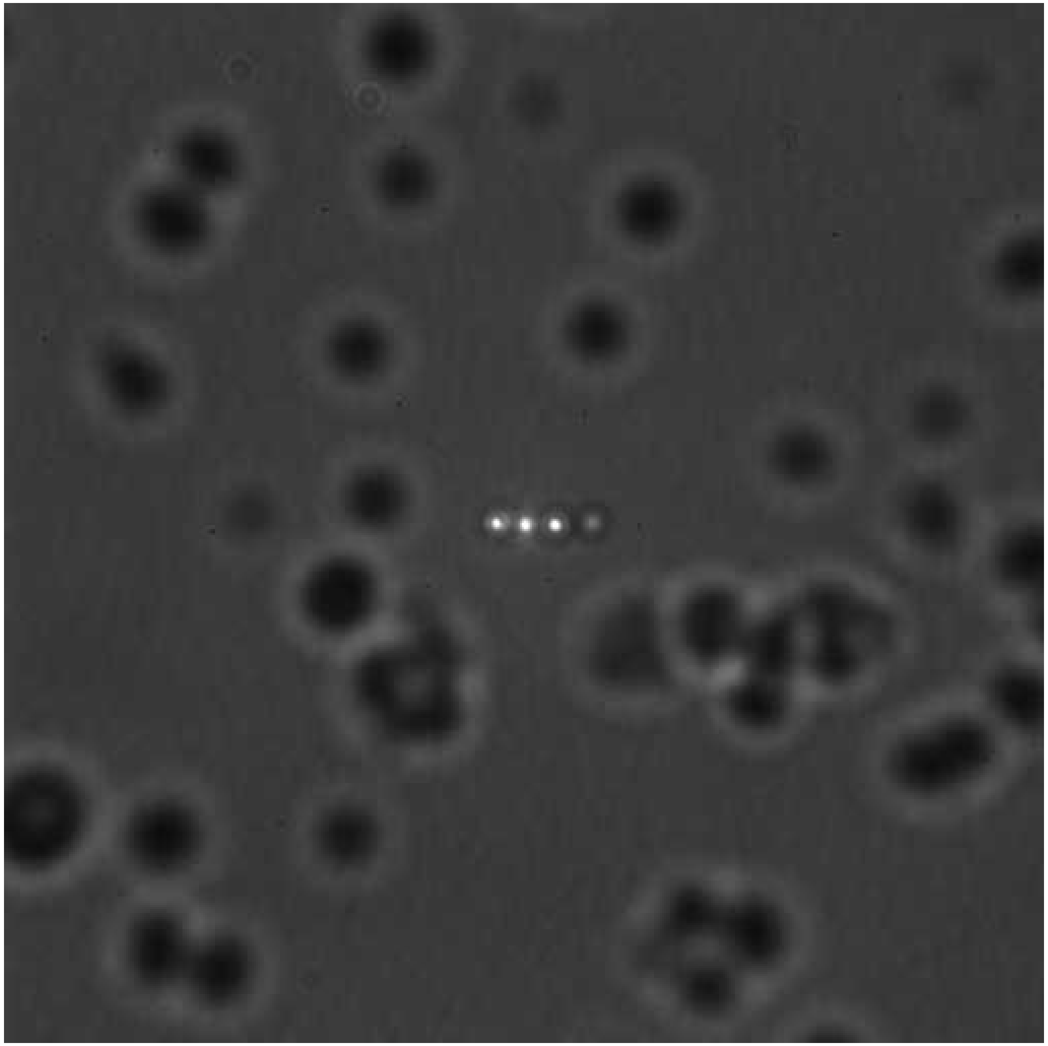
Borosilicate Particles with SP-MMA Layers

- A higher particle refractive index is required for optical trapping in toluene (n = 1.49).
- Particles of borosilicate glass (~2 micron) were coated with 20% SP-MMA layers to created photochromic responses. (n = 1.56)
- The layer thickness is estimated for these particles at ~ 100 nm.





Optical Trapping of Photochromic Particles



- Three optical traps are active in this line of particles.
- The fourth particle is not trapped.
- A flow cell design is being used to inject more particles into the system.
- Once assembled, the structure diffuses as a single entity, and can be moved to the desired position.
- Work to ordered structures is ongoing.

Conclusions

1. Photochromic molecules show the capability to influence surface wetting and colloidal stability.
2. Changes in optical and surface energy of modified surfaces have been detected by UV/VIS and contact angle measurements, respectively.
3. Modeling of Surface Energy Parameters gives greater insight into the mechanisms of surface energy control and allows screening of systems to generate desired photowetting effects.
4. A colloidal system has demonstrated reversible aggregation and dispersion phenomena.
5. Polymer layers show greater cycle lifetime than monolayers.
6. Optical Trapping is being pursued for the formation of colloidal structures with non-equilibrium or close packed nature.

Acknowledgements

Additional contributors:

- Marcin Piech, United Technologies Corporation
- Dongqing Yang and Tom Picraux, University of Arizona, CINT
- Matt George and Paul Braun, UIUC
- Anne Grillet, Chris Brotherton, Tim Koehler, Greg Jamison, Chad Staiger, Sandia National Laboratory

Facilities:

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

Funding:

- LDRD and NINE Programs at Sandia National Laboratory
- Army Research Office – MURI Grant
- Department of Energy