

# Directed Assembly of Non-Equilibrium Structures Utilizing Optical Trapping and Surface-Modified Colloids

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# Motivation

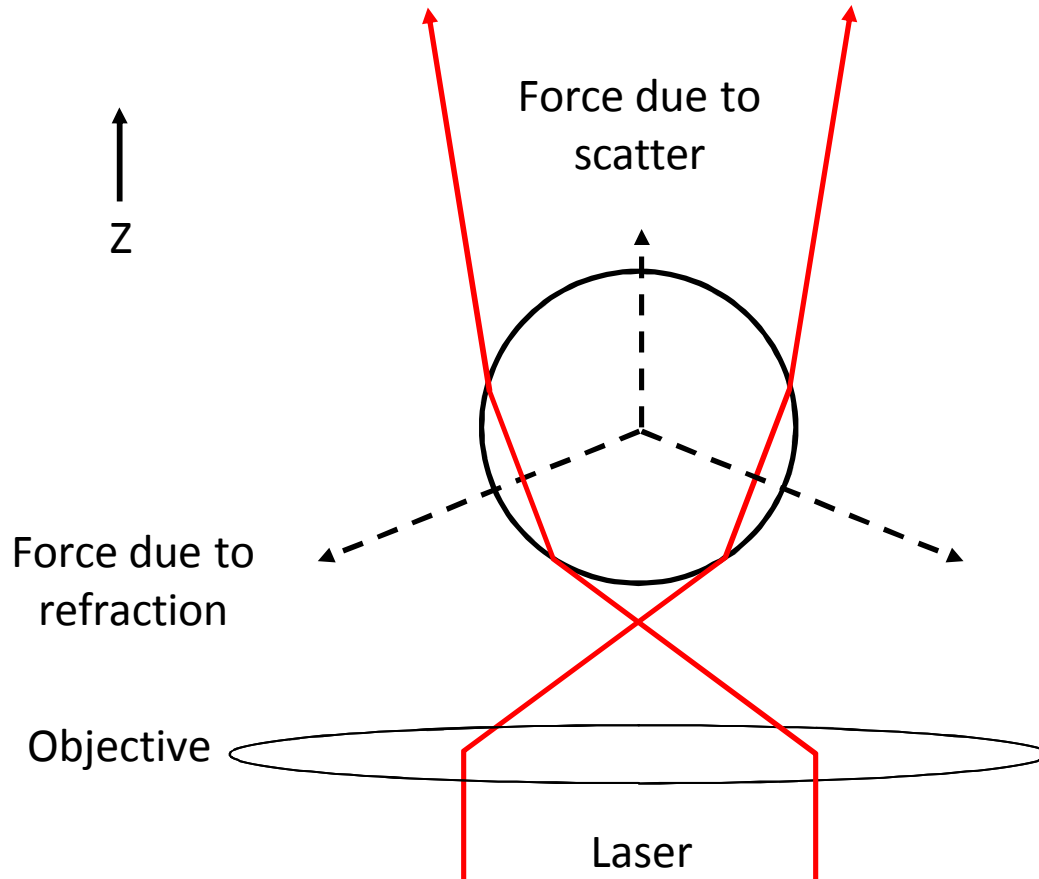
Non-equilibrium microstructures could be used to develop novel materials with interesting optical and/or thermal properties

Directed assembly of photosensitive particles could result in a multitude of unique microstructures

# Objective

Develop a technique to assemble non-equilibrium structures using optical tweezers for alignment and surface chemistry to lock-in the aligned structure.

# Optical Trapping



- 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  $\rightarrow$  easier to trap particles.

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

# 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

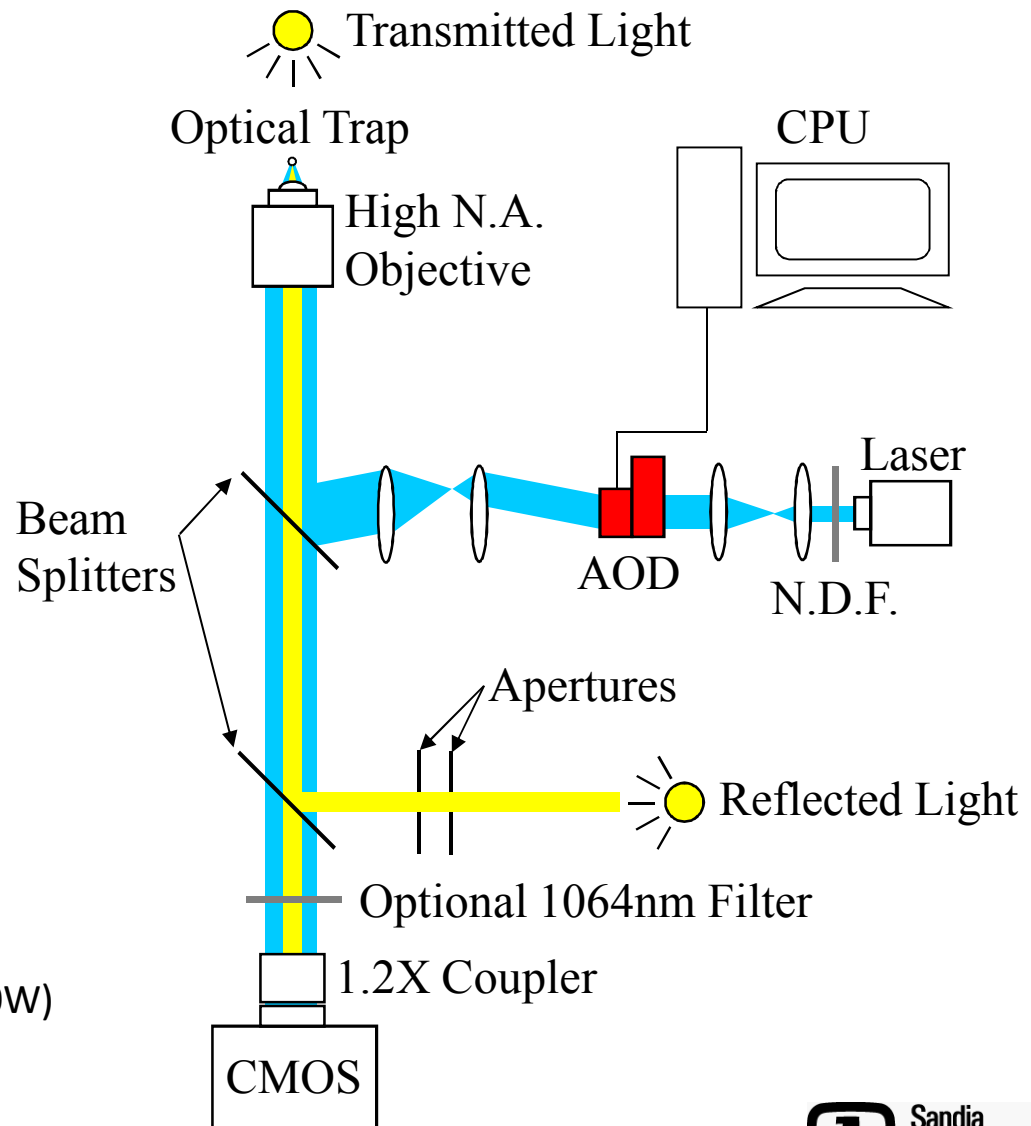
- Nikon TE2000-S
- Prior ProScan II Motorized Stage

## High N/A Objective

- Nikon Plan Fluor 100x/1.3 Oil Immersion

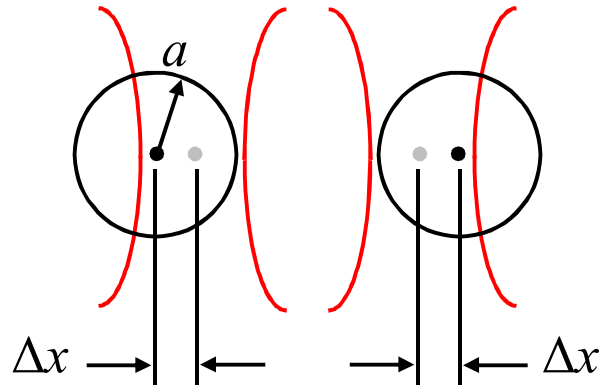
## Reflected Light

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



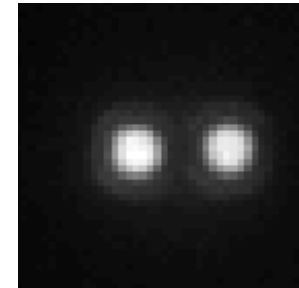
# Optical Trapping Applications

## Particle Interactions

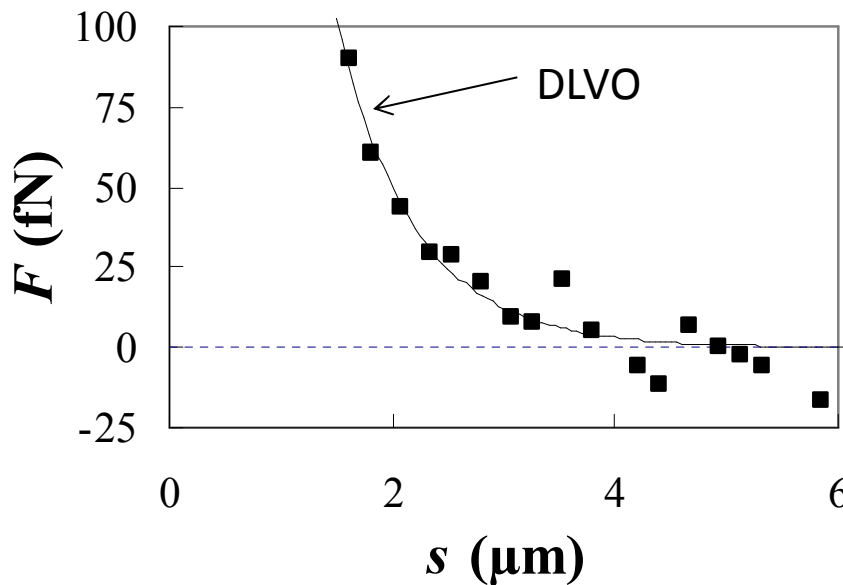


Hookean Force

$$F = k\Delta x$$

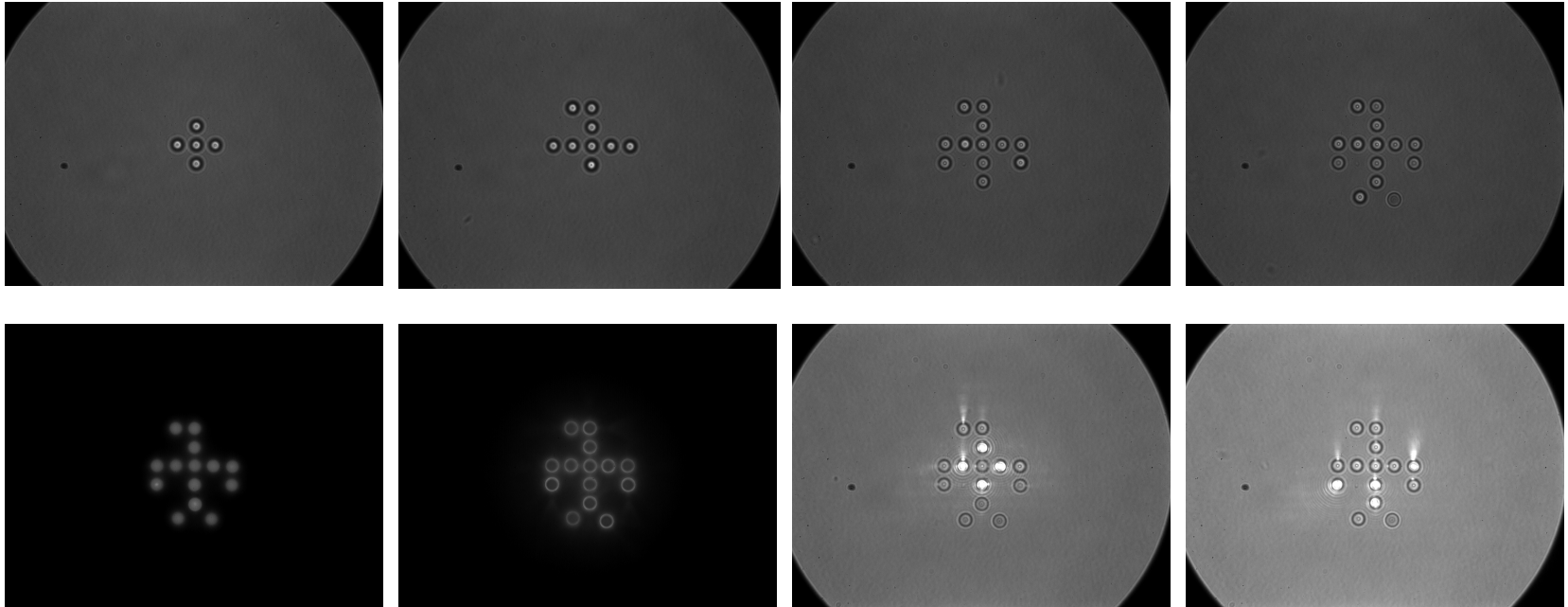


### Force Versus Separation

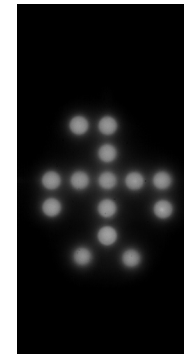


2.4 micron Carboxyl-Modified Polystyrene Microspheres in 1mM AOT/Hexadecane

# Multiple Optical Traps Allow for Precise Orientation of Silica Particles



- This structure is built using 14 time-shared optical traps.
- These particles are fluorescent polystyrene in water.
- Particles are “caught” by Brownian diffusion into the field of view, and maintained in the position desired by the optical trap.



# Strategic Approach to forming a Photosensitive Colloidal System

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

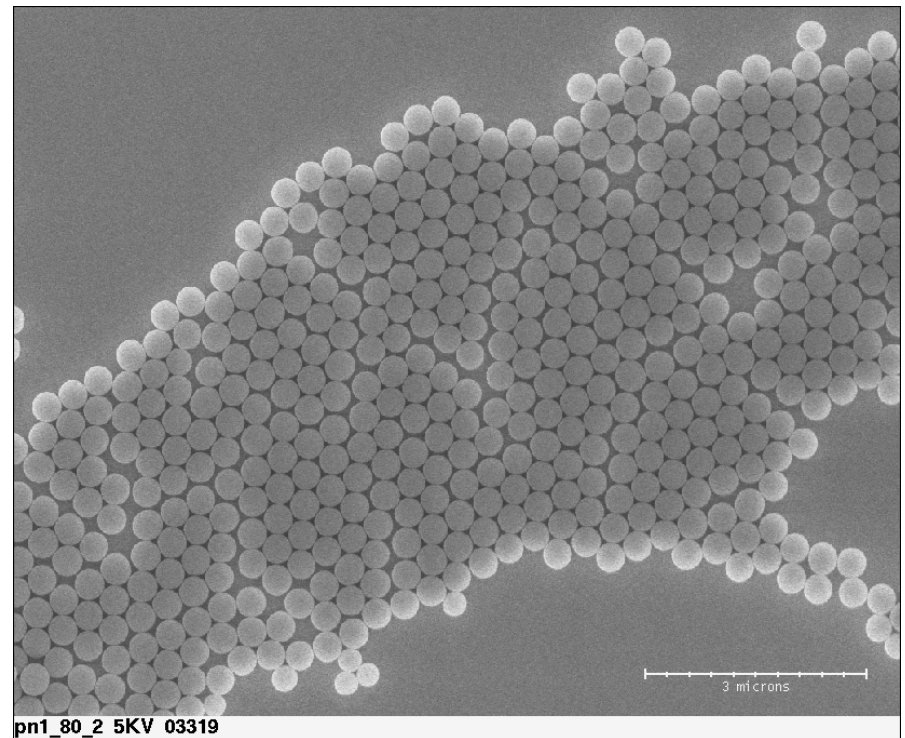
Particle system: Silica

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

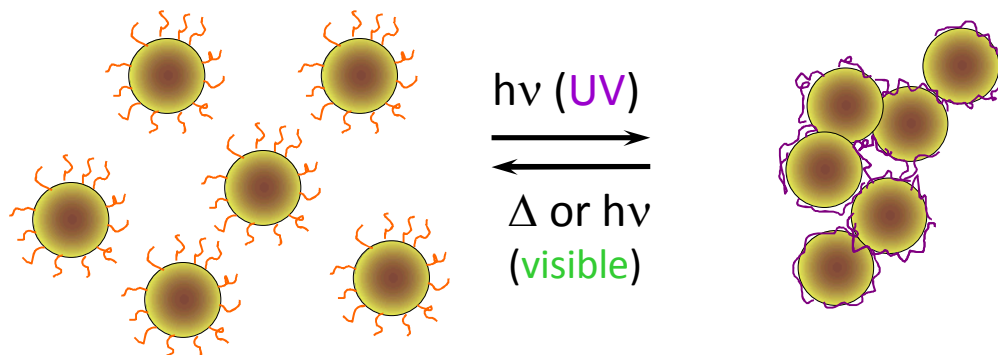
Organic component: spiropyran

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

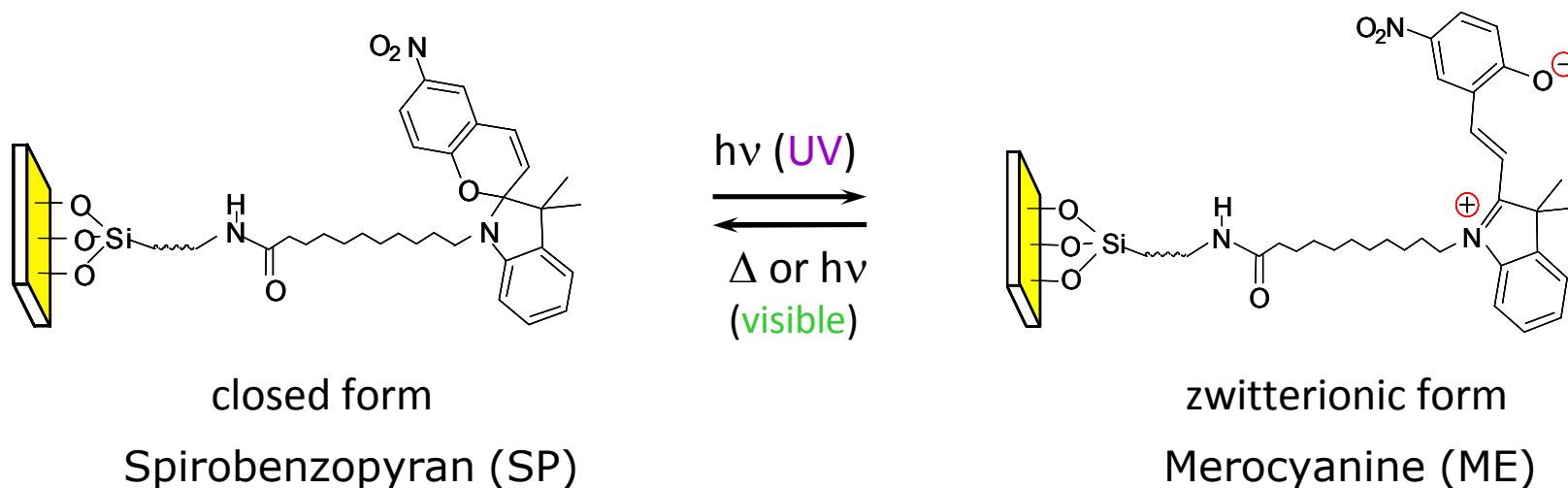
Approach: Derivatize particles with layers of photo-switchable polymer.



# Reversible Light-regulated Colloidal Interactions



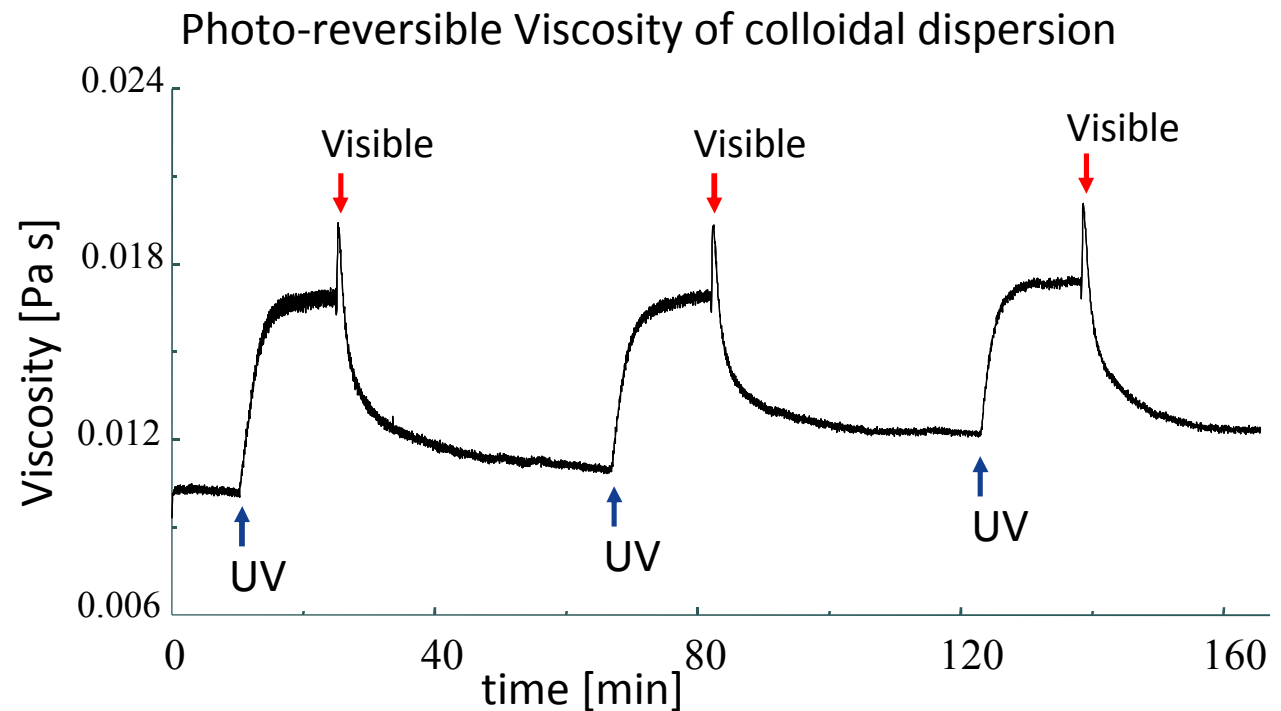
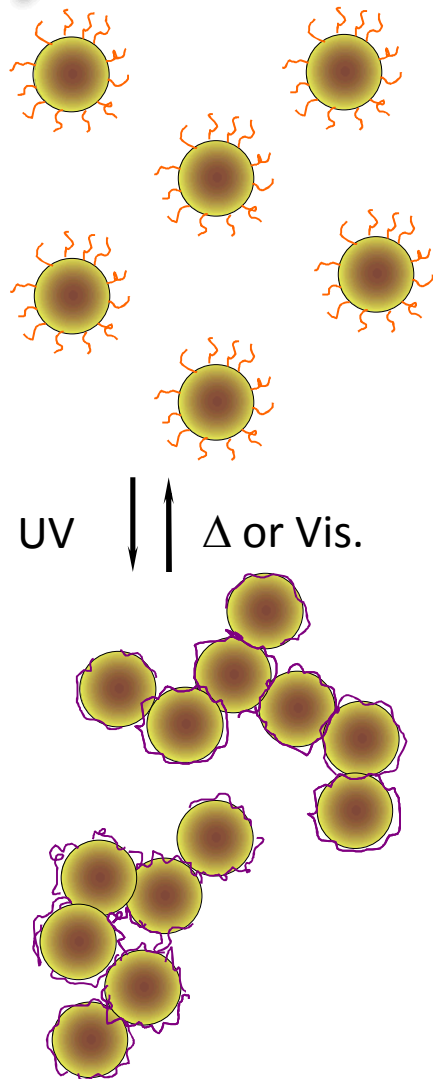
**Approach:** Utilize reversible photochemical reaction



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



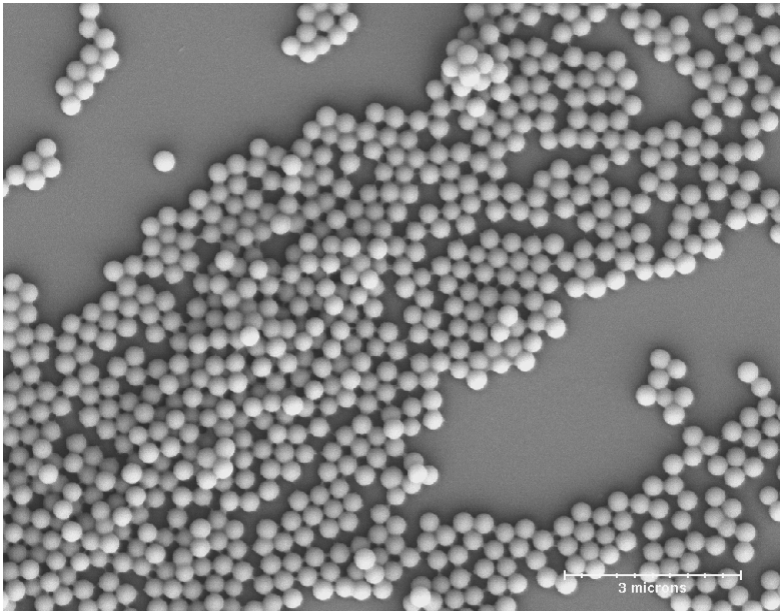
# Photo-control of Viscosity in Colloidal Systems



1  $\mu\text{m}$  SP/MMA modified colloids (20% SP) in toluene at  $\sim 30$  vol.%

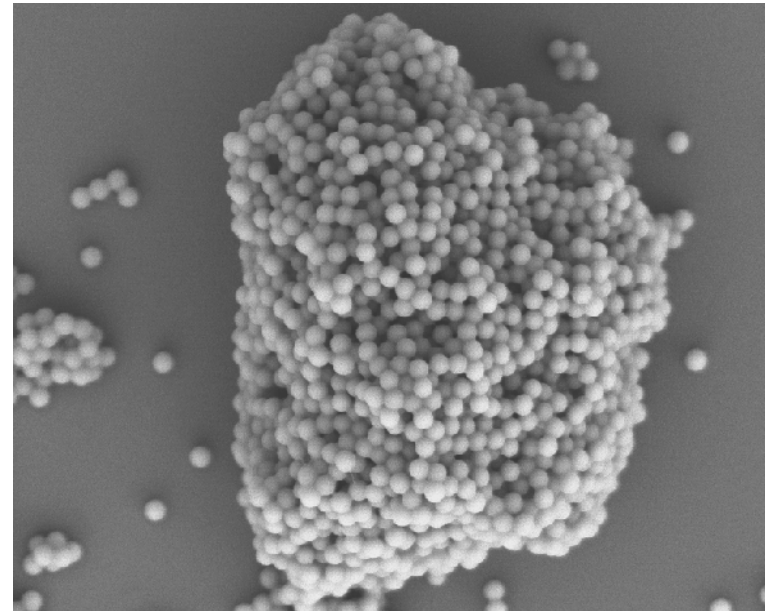
# Sediment Comparison via SEM

No UV exposure



Particles form well spread mono- and multi-layer predominant hexagonally packed domains

After 1 min UV irradiation ( $\lambda=366$  nm)



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

# Photoaggregation of SP-MMA Particles in Toluene

no UV  
exposure

after  
1 min UV



time = 5 sec  
after shaking



time = 30 sec



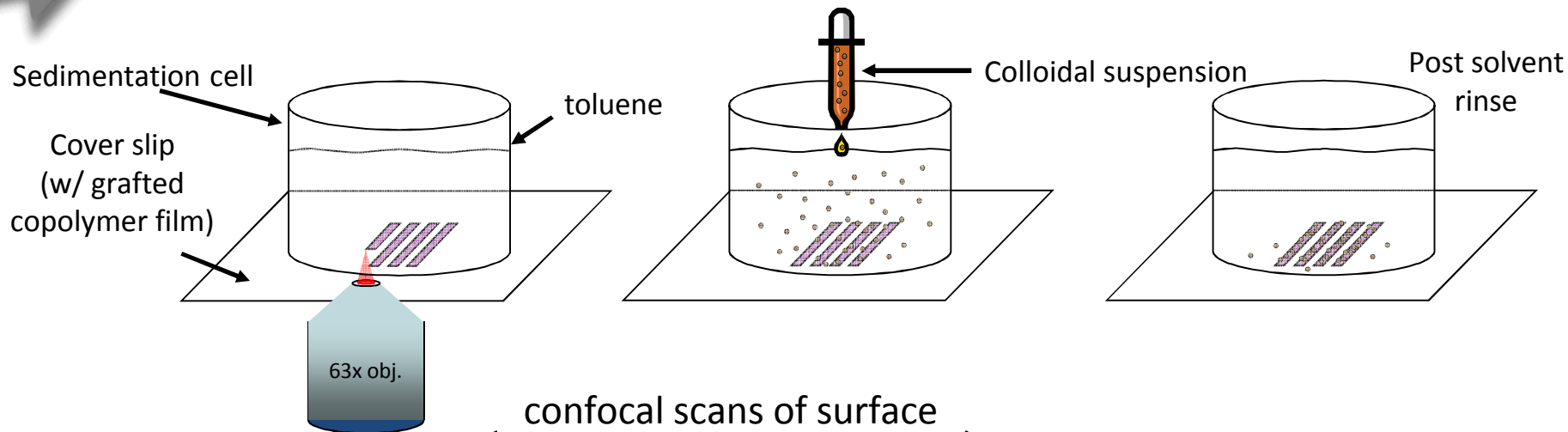
time = 45 sec



time = 90 sec

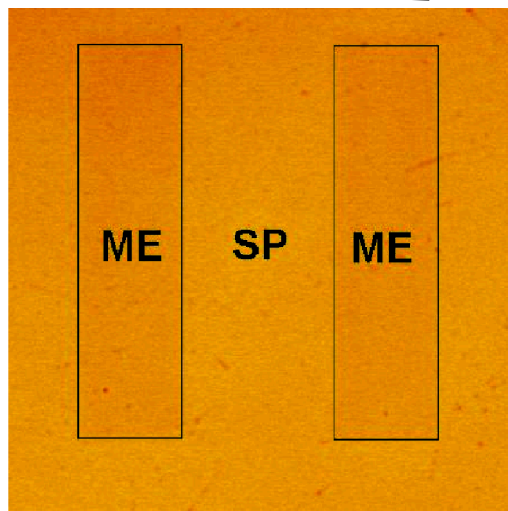
- SP molecules in non-polar, closed form particles are yellow and well dispersed
- UV exposure ( $\lambda=366$  nm) induces aggregation with SP molecules now in polar, open form; purple particle aggregates quickly sediment

# 2D Photo-defined Colloidal Adsorption

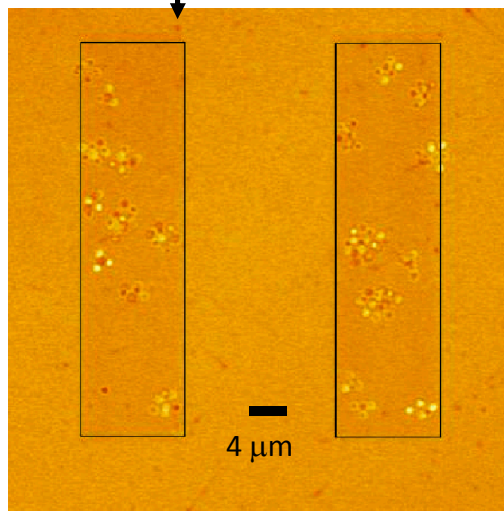


confocal scans of surface

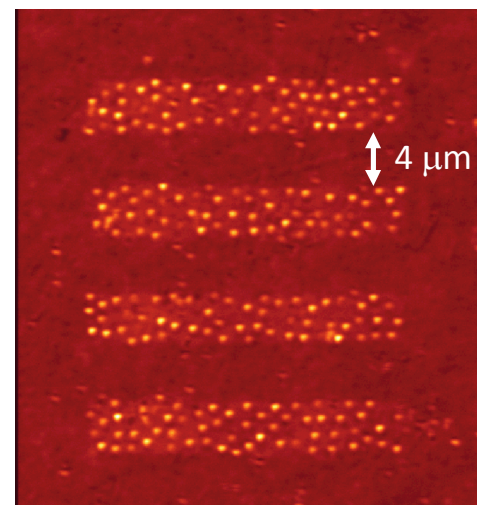
2D patterning example



exp. start,  $t = 0$

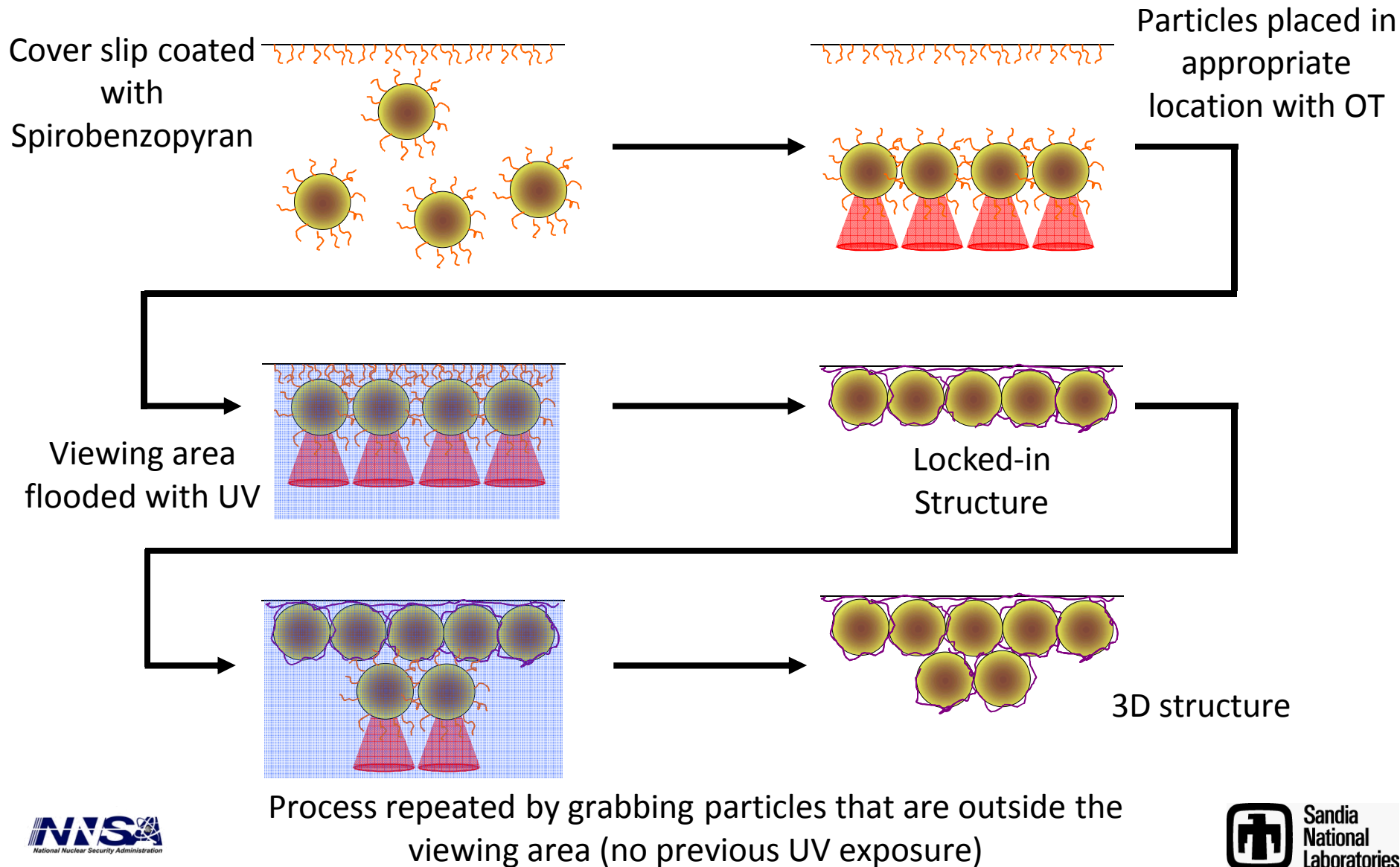


clusters,  $t = 660 \text{ s}$



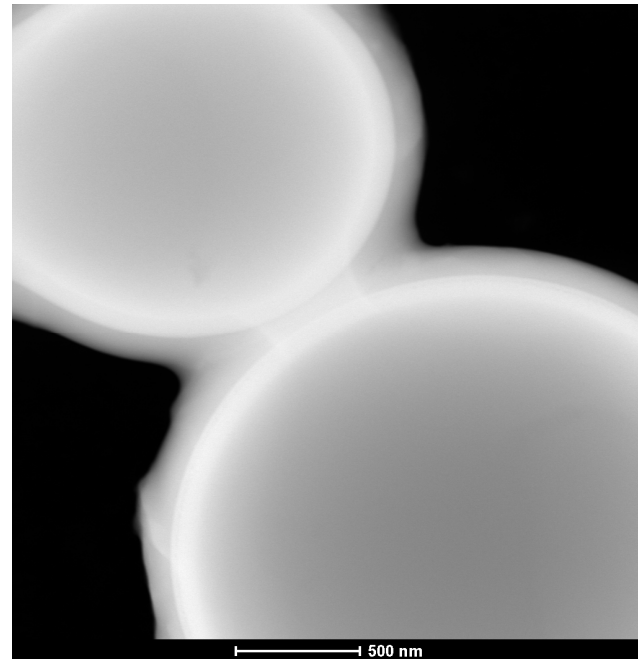
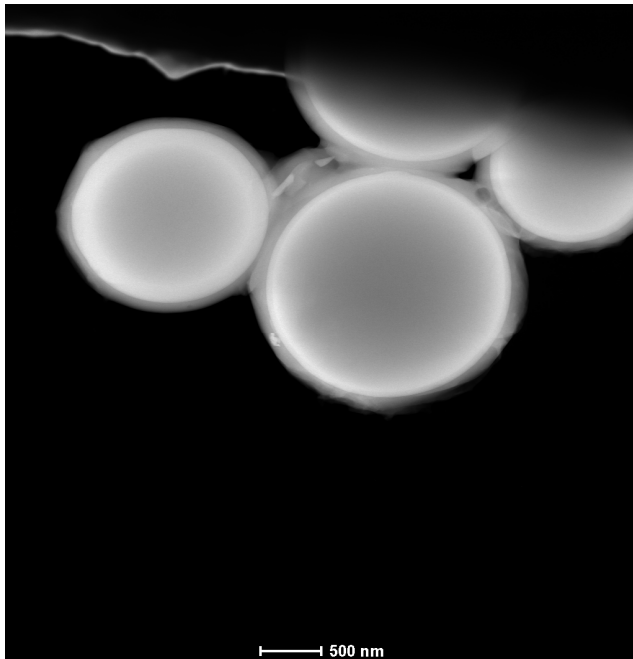


# Route to Structure Fabrication using SP-MMA Functionalized Particles

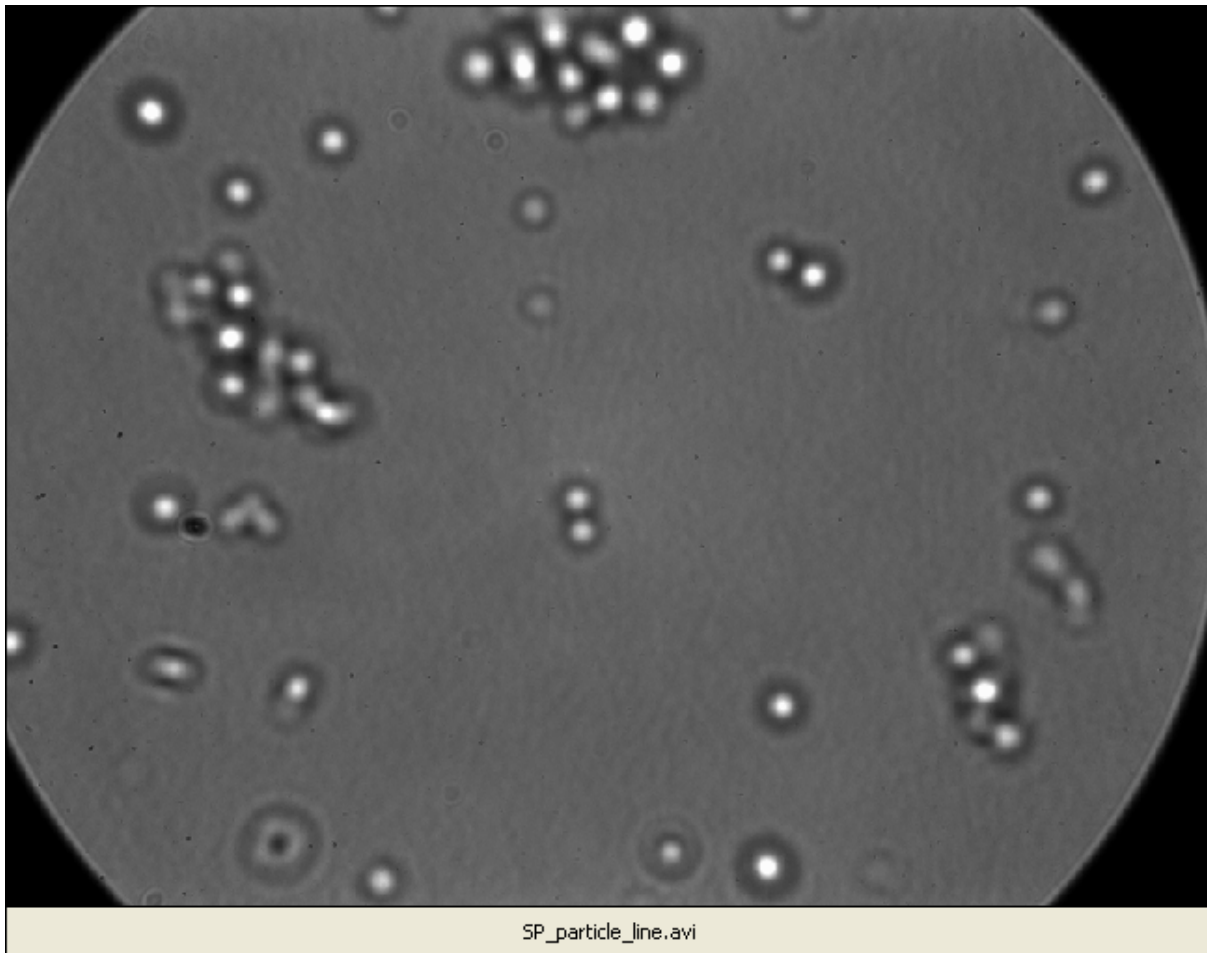


# Borosilicate Particles with SP-MMA Layers

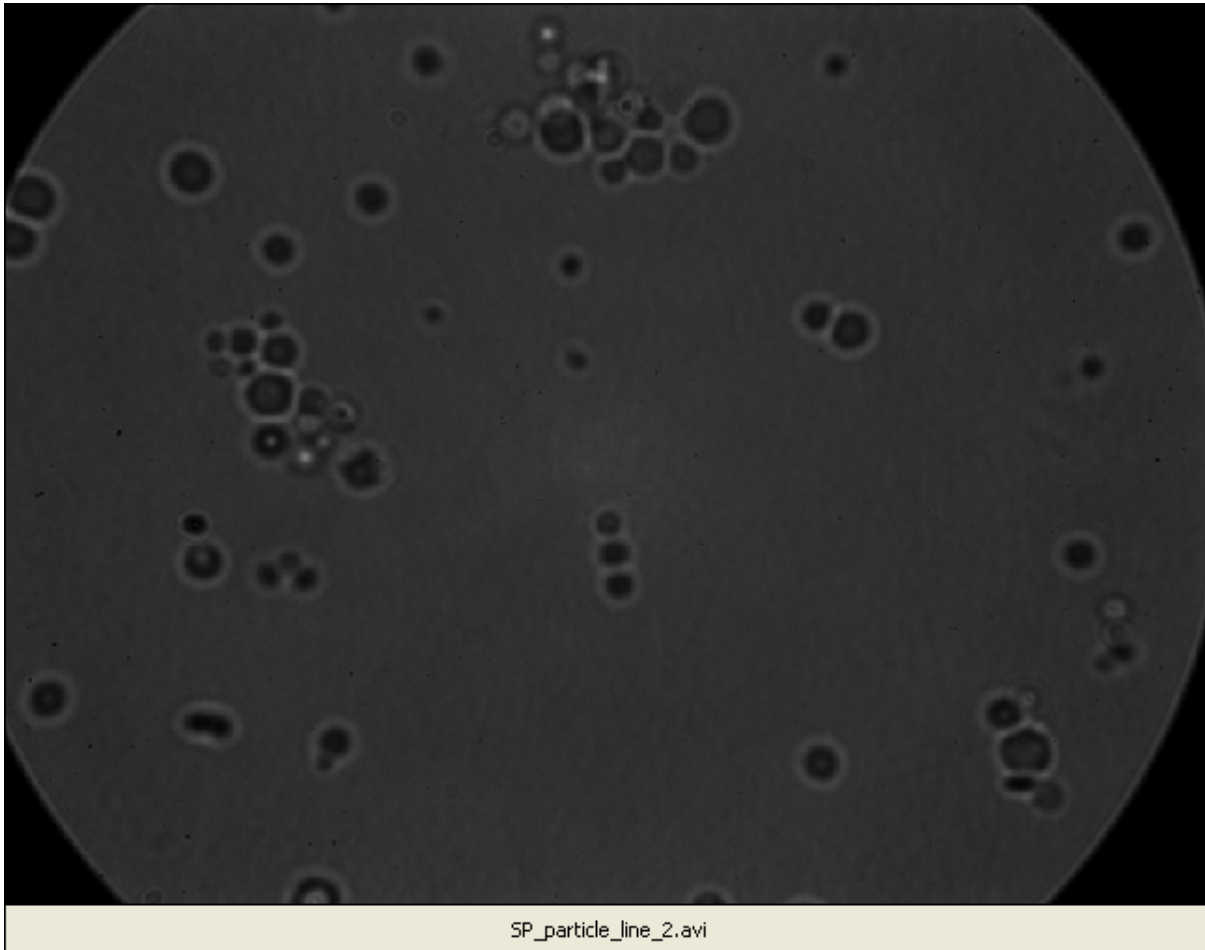
- A higher particle refractive index is required for optical trapping in toluene ( $n = 1.49$ ).
- Particles of borosilicate glass ( $\sim 2$  micron) were coated with 20% SP-MMA layers to create photochromic responses. ( $n = 1.56$ )
- The layer thickness is estimated for these particles at  $\sim 100$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



# Optical Assembly of Photochromic Particles

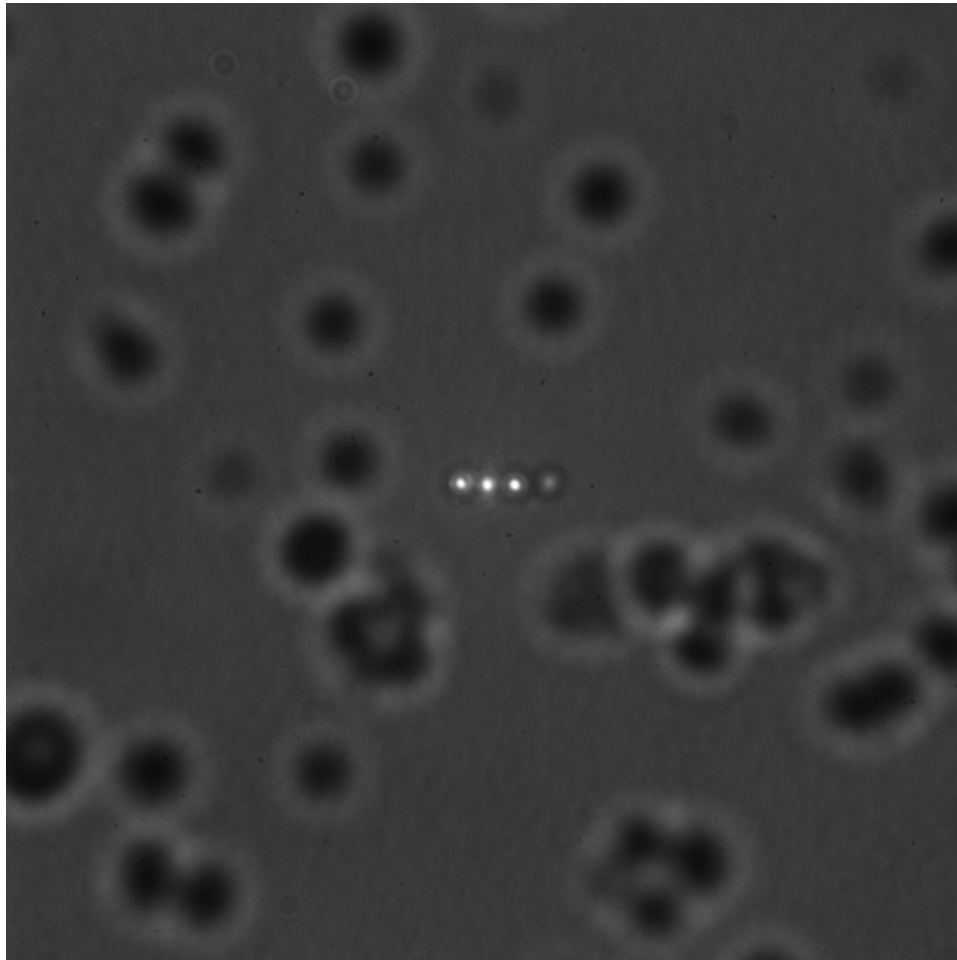


# Optical Assembly of Photochromic Particles



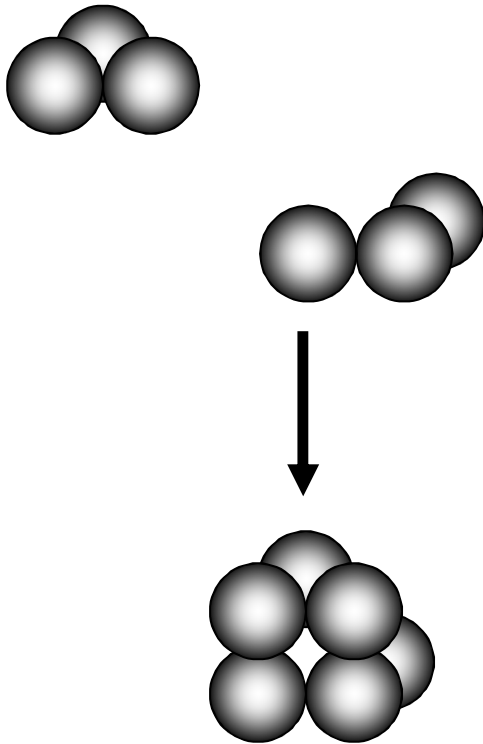


# Optical Trapping of Photochromic Particles



- 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.

# Microstructure Assembly using Optical Trapping





# Conclusions

## Successes:

- Photosensitive chemistry can be used to control aggregation of microparticles
- Optical tweezers enable manipulation of particles into non-equilibrium positions
- 3D assembly was possible using borosilicate particles coated in Spyrobenzopyran in toluene

## Difficulties:

- Spyrobenzopyran brushes are very sensitive to UV and lead to premature agglomeration
- Borosilicate/Toluene system is challenging due to settling

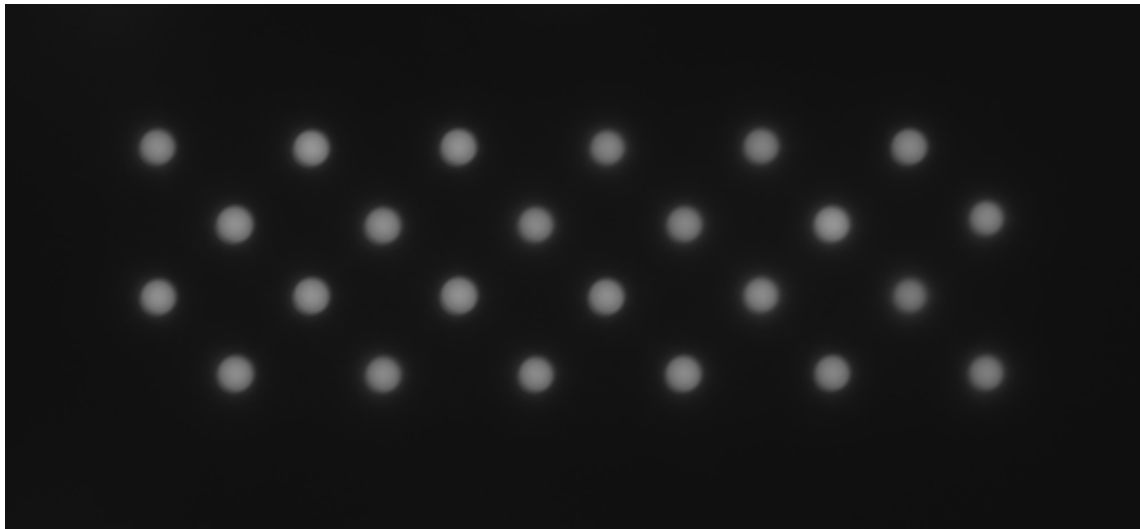
## Path forward:

- Holographic optical tweezers are capable of 3D particle manipulation and thus assembly
- Identify lower refractive index solvents to better density match particle/solvent system



# Future Work

## 3D Positioning using Holographic Optical Trapping (HOT)





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