

Nanoparticles at Soft Material Interfaces

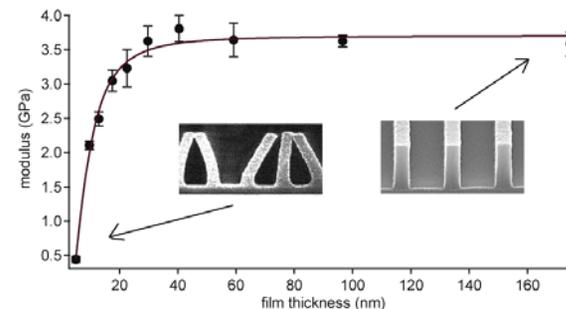
Jason J. Benkoski, Joong Tark Han, Brian Berry
Alamgir Karim

NCMC-9
Monday, April 24th 2006

Nanostructured Materials Group

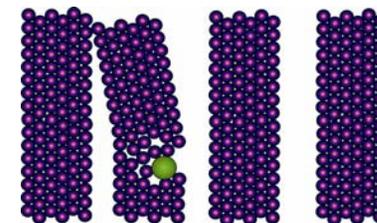
Nanoimprint Lithography

- Addresses fundamental imprint metrology issues
- Metrology for manufacture of robust nanostructures
- Relate nanomanufacturing processes with structure and stability



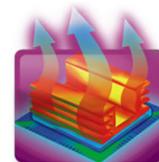
Defects in Polymer Nanostructures

- Critical defects issues related to nanomanufacturing
- Develop metrology for 3-D characterization of defects in nanostructures
 - Methods to control defects in self-assembling polymeric systems
 - Metrology with nanoprobes to quantify interactions and defects



Thermal Management in Nanodevices

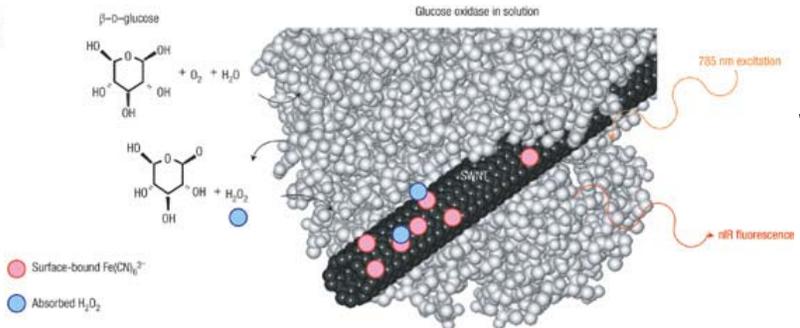
- Address critical problem of shrinking device dimension vs. increasing power dissipation
- Develop metrology for thermal and dielectrics response in nanodevices
- Develop metrology for simultaneous measurement of thermal conductivity, complex heat capacity, interfacial thermal resistance, and dipolar relaxation spectra



Outline

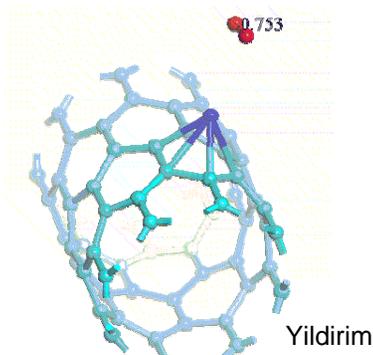
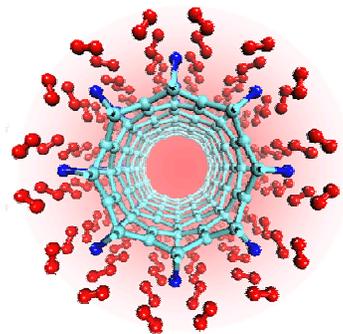
- Biomimetic Surface Processing
 - Oil/water interface
 - Nanoparticle-mediated processing
 - Hierarchical topology → superhydrophobicity
 - Particle aggregation
 - » Aggregation vs. Dispersion
 - » Flocculation vs. Self-Assembly
- Particle/Surface Interaction
 - Effect of chemistry
 - Effects of topology

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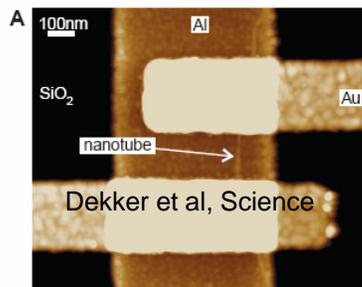
Sensing

Ammonia, methane, acetone, glucose...



Energy

electro-catalyst support fuel-cell electrodes
hydrogen storage materials



Electronics

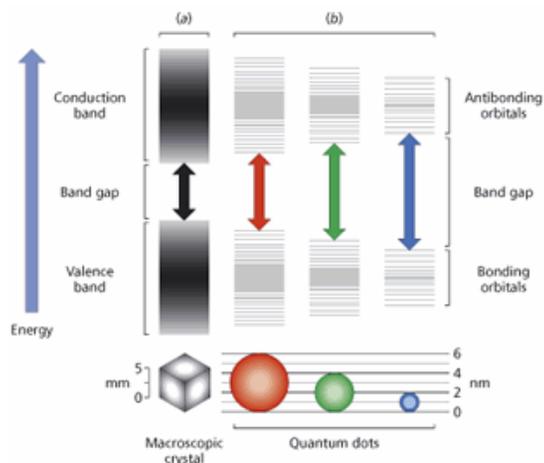
Metallic and semiconducting
FETs, memory, logic circuits

Future Applications Important to US Manufacturing Sectors

Dendrimers



Quantum Dots

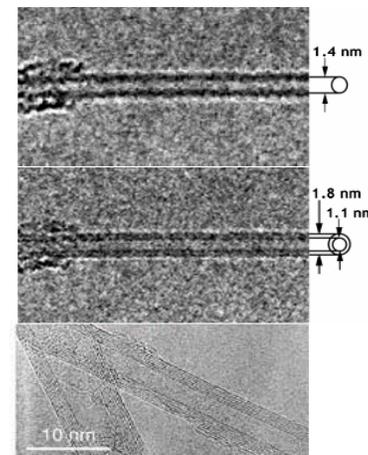


Nanotubes (C, Au, Hybrid...)

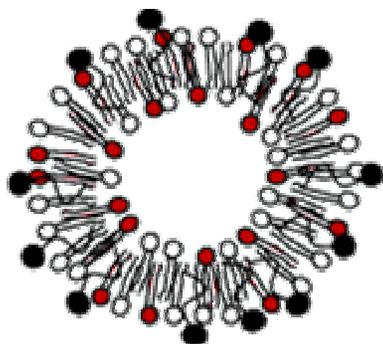
SWNT

DWNT

MWNT



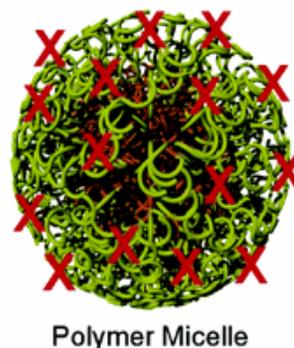
Liposomes



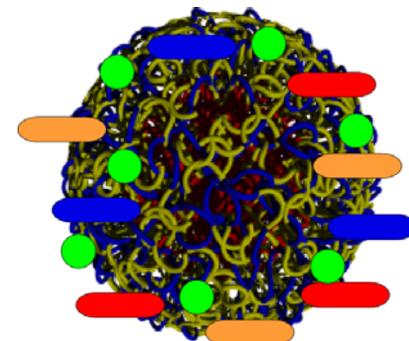
Micelles



Micelle
Formation



Nanoparticles



Diversity of Nanoparticles Presents
Numerous Characterization Challenges

Advanced Functional Surfaces

Lotus Leaf

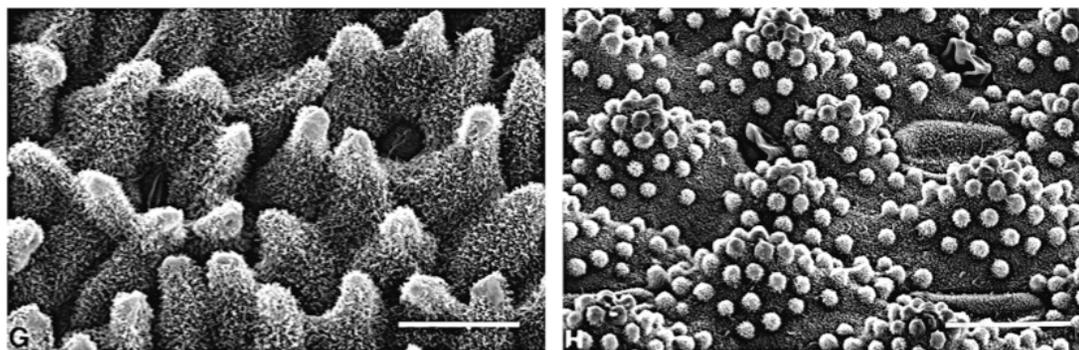
Superhydrophobic

Self-cleaning

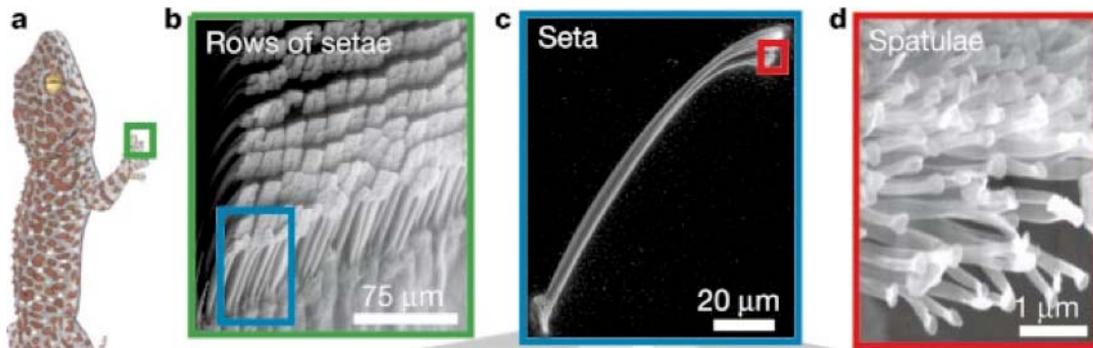
Gecko Feet

Superadhesive

Self-Cleaning

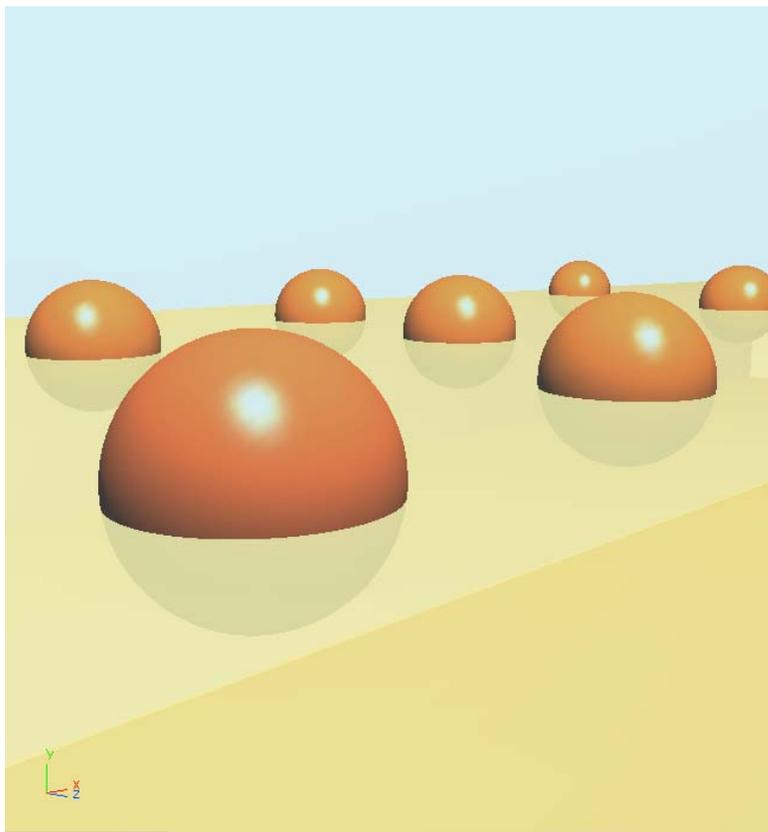


SEM micrographs of lotus leaf surfaces

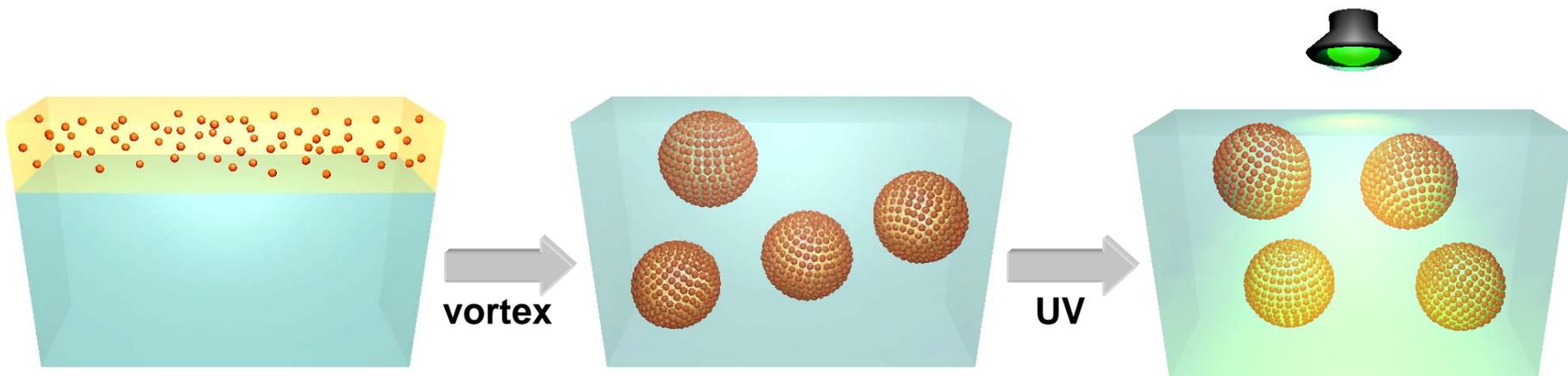


SEM micrographs of gecko feet surfaces at many
length scales

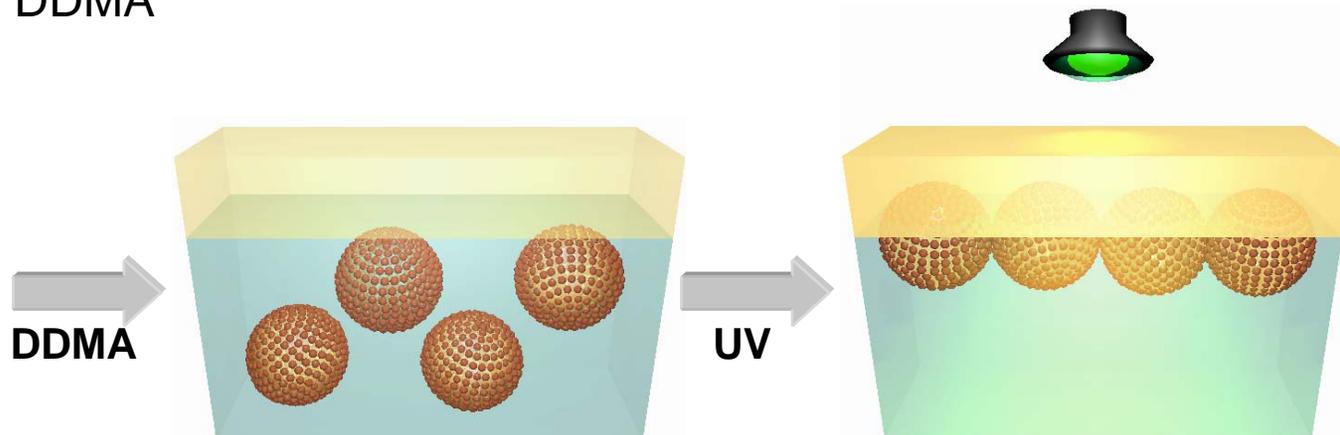
Biomimetic Processing



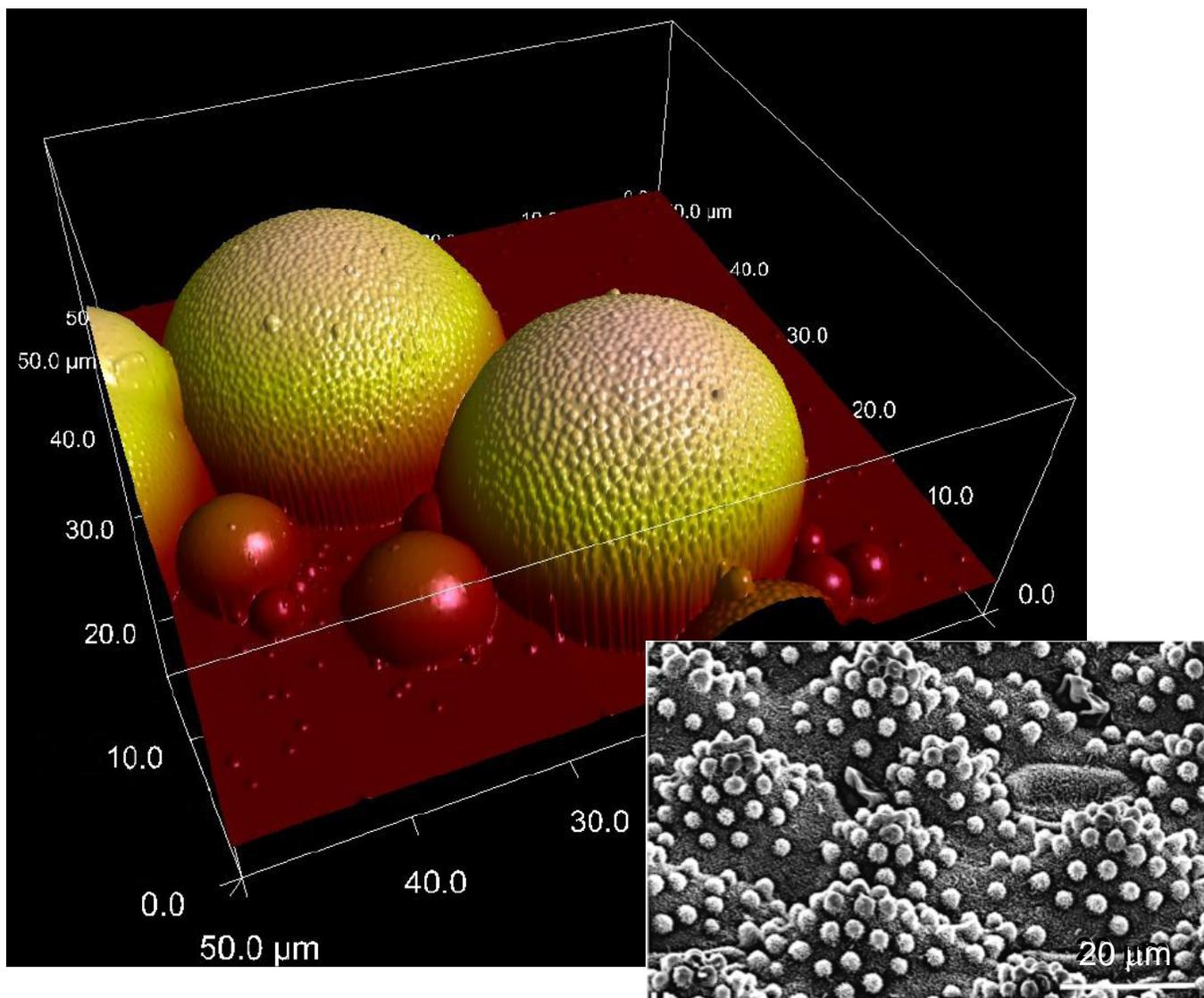
- Biomimetic Surface Processing
 - Extraordinary properties from ordinary materials
 - Primary characteristics
 - aqueous environment
 - minimal waste
 - low energy
 - low cost
 - *Use an oil/water interface where the oil can flash-cure in less than 1 s*



390 nm PMMA
particles (5 wt %) in
DDMA

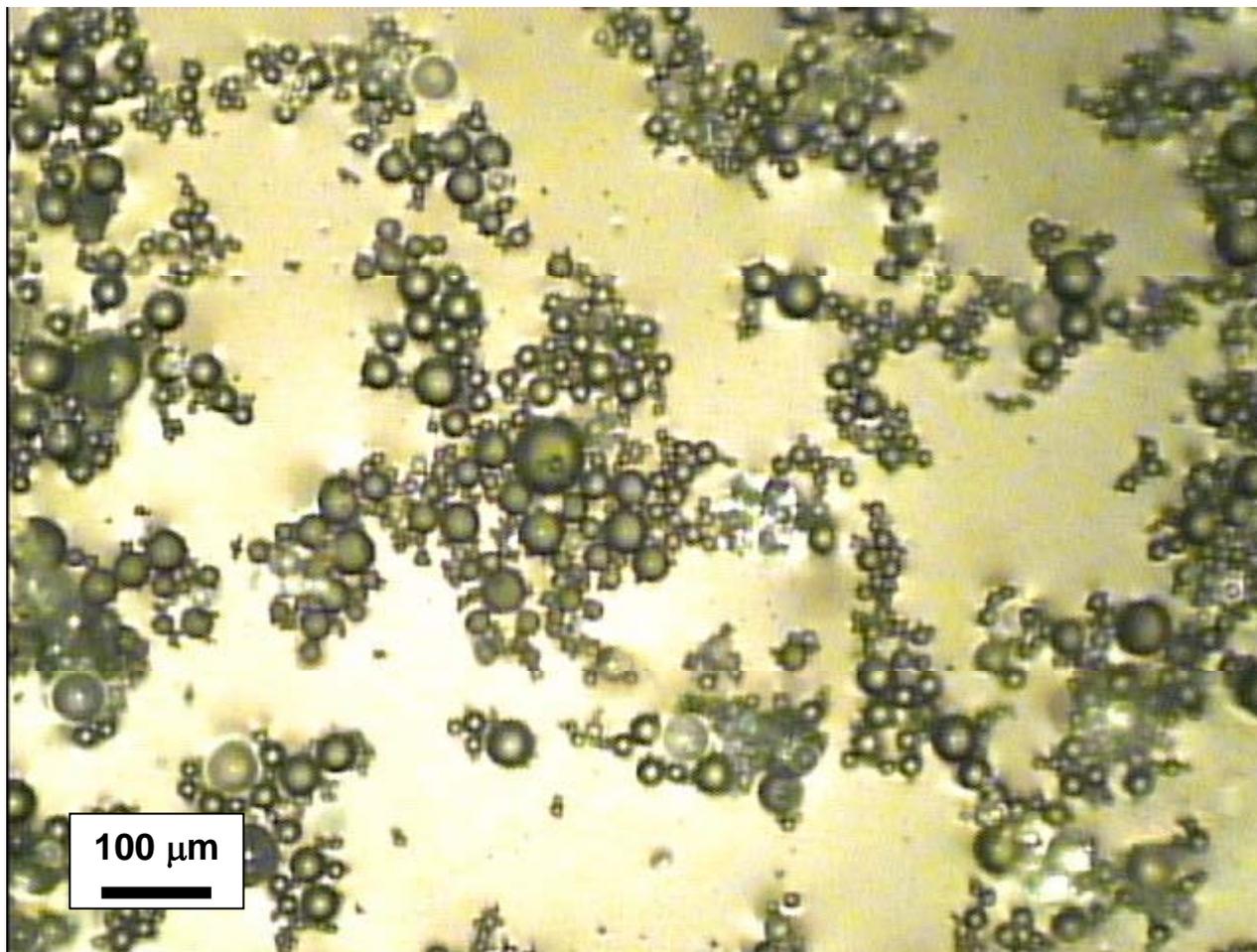


Colloidosome Preparation



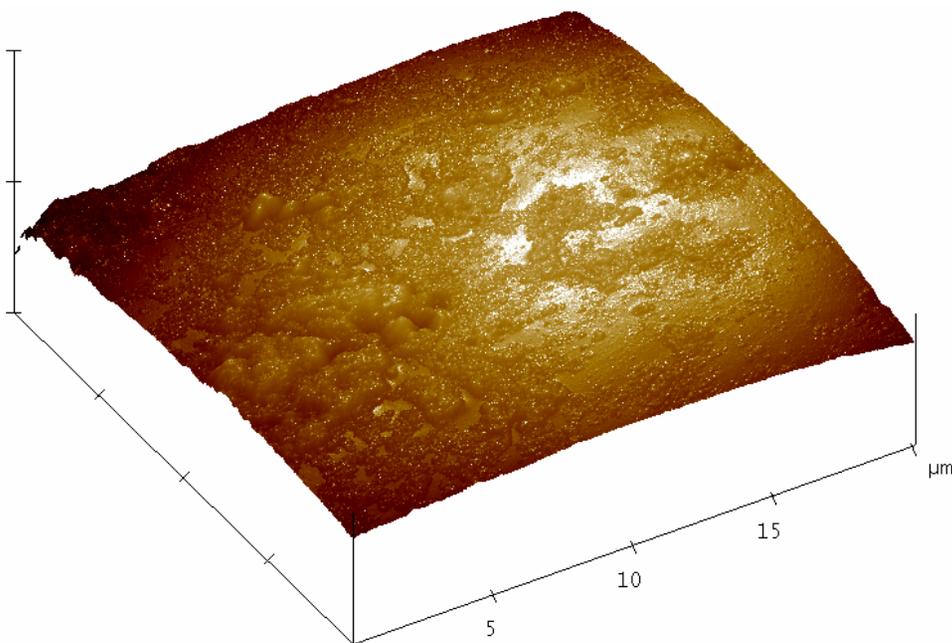
Neinhuis, C.; Barthlott, W. *Annals Bot.* **1997**, *79*, 667.

Hierarchical Topology

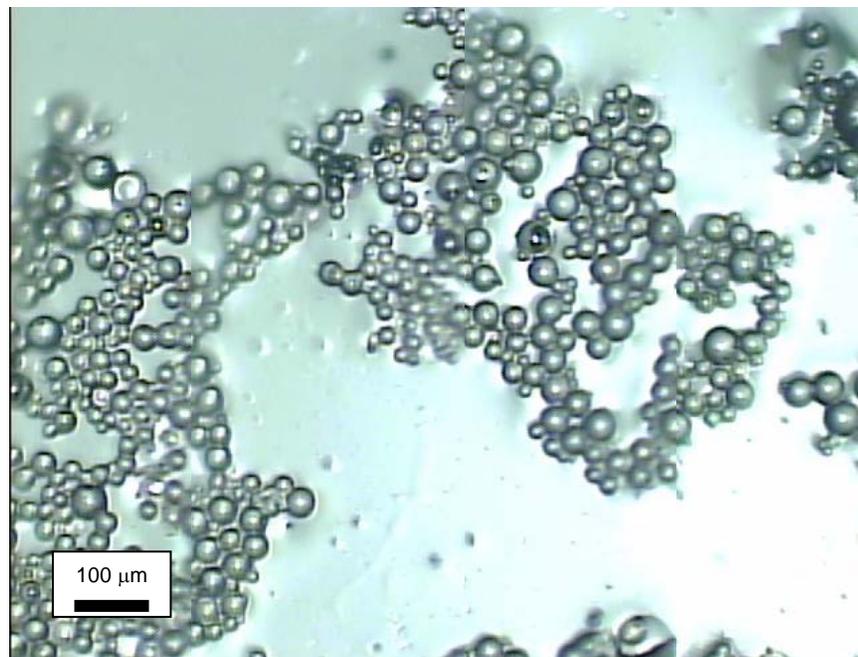


Multiple Length Scales

Replace 390 nm PMMA particles with 25 nm magnetite nanoparticles and repeat same process

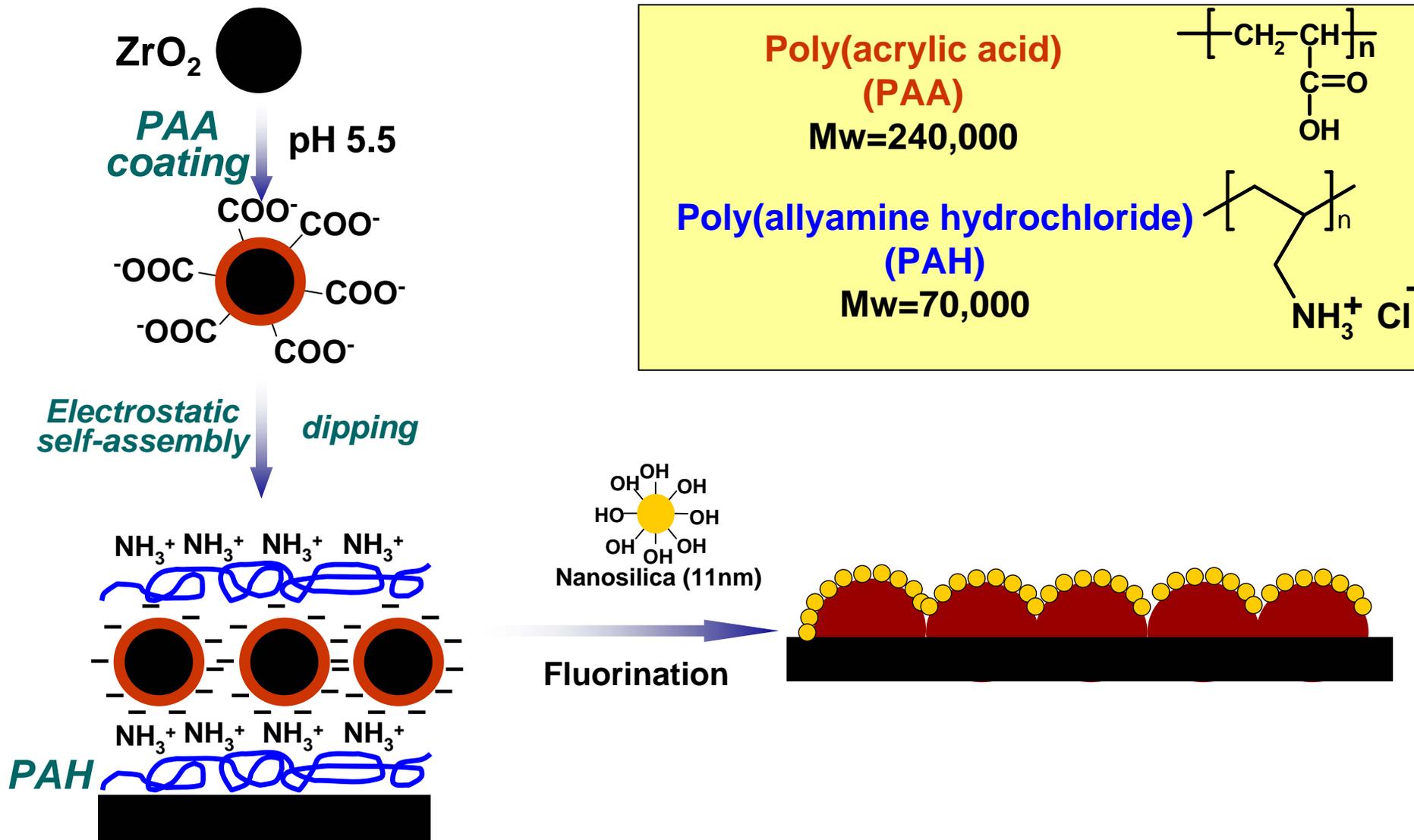


Fe_3O_4 segregates to the colloidosome surface in irregular aggregates

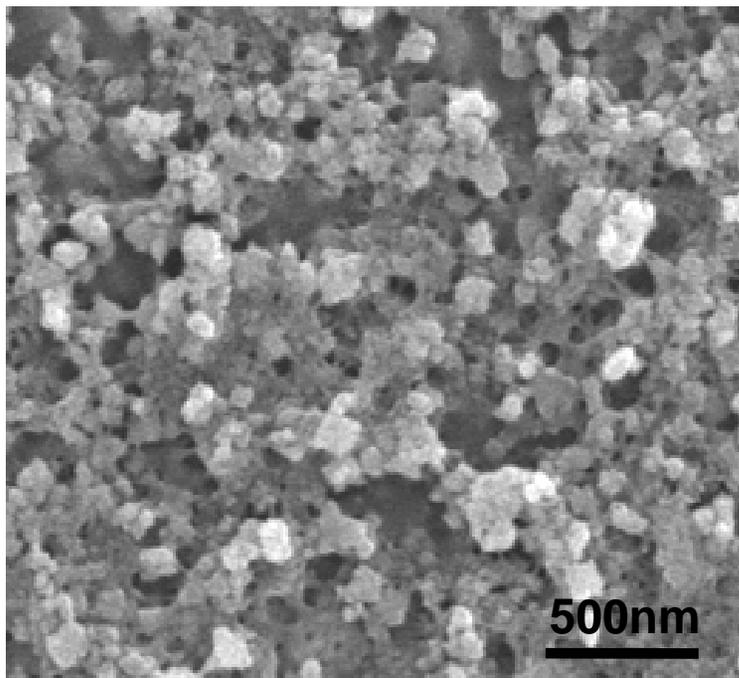


Magnetic colloidosomes

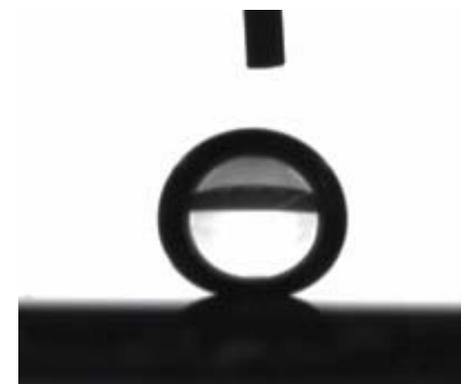
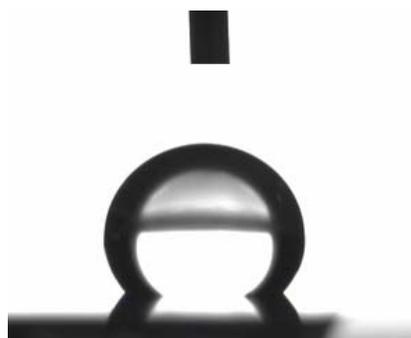
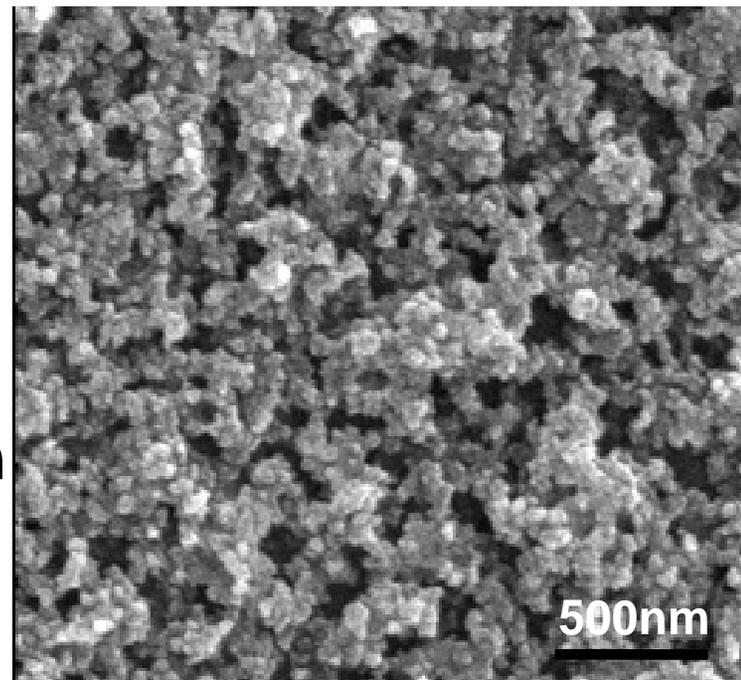
Other Particle Types



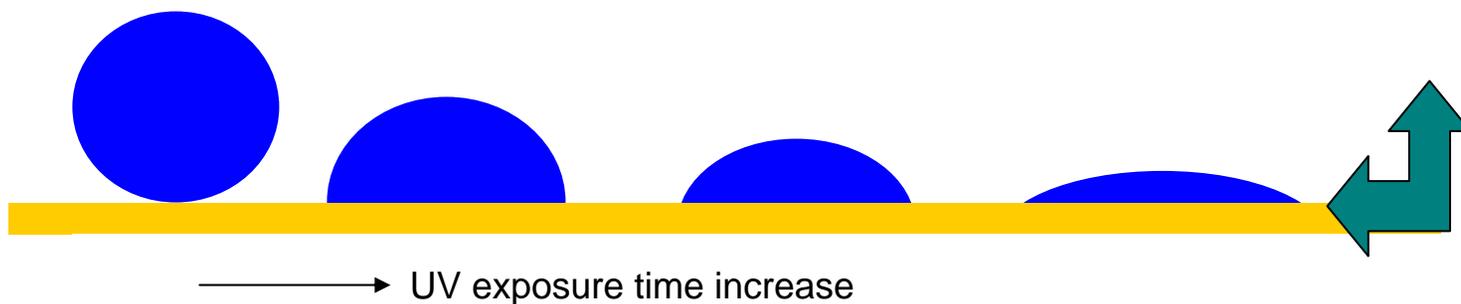
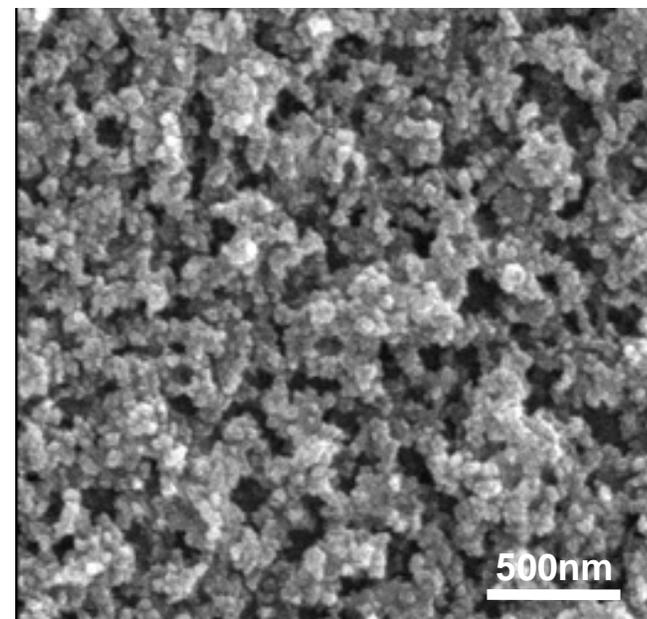
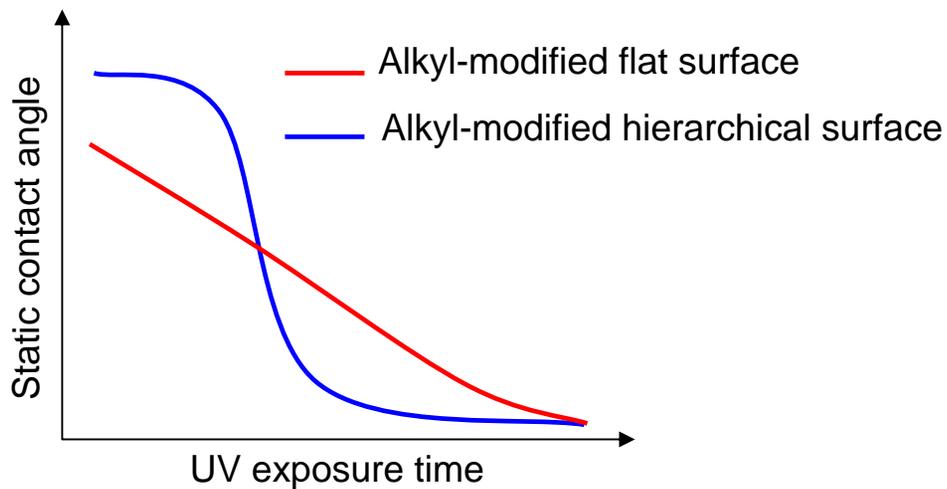
Stable Superhydrophobic Organic/Inorganic hybrid films using electrostatic self-assembly

$(\text{PAH/PAA-ZrO}_2)_{10}$ 

Nanosilica
($d=11\text{nm}$)
→
fluorination



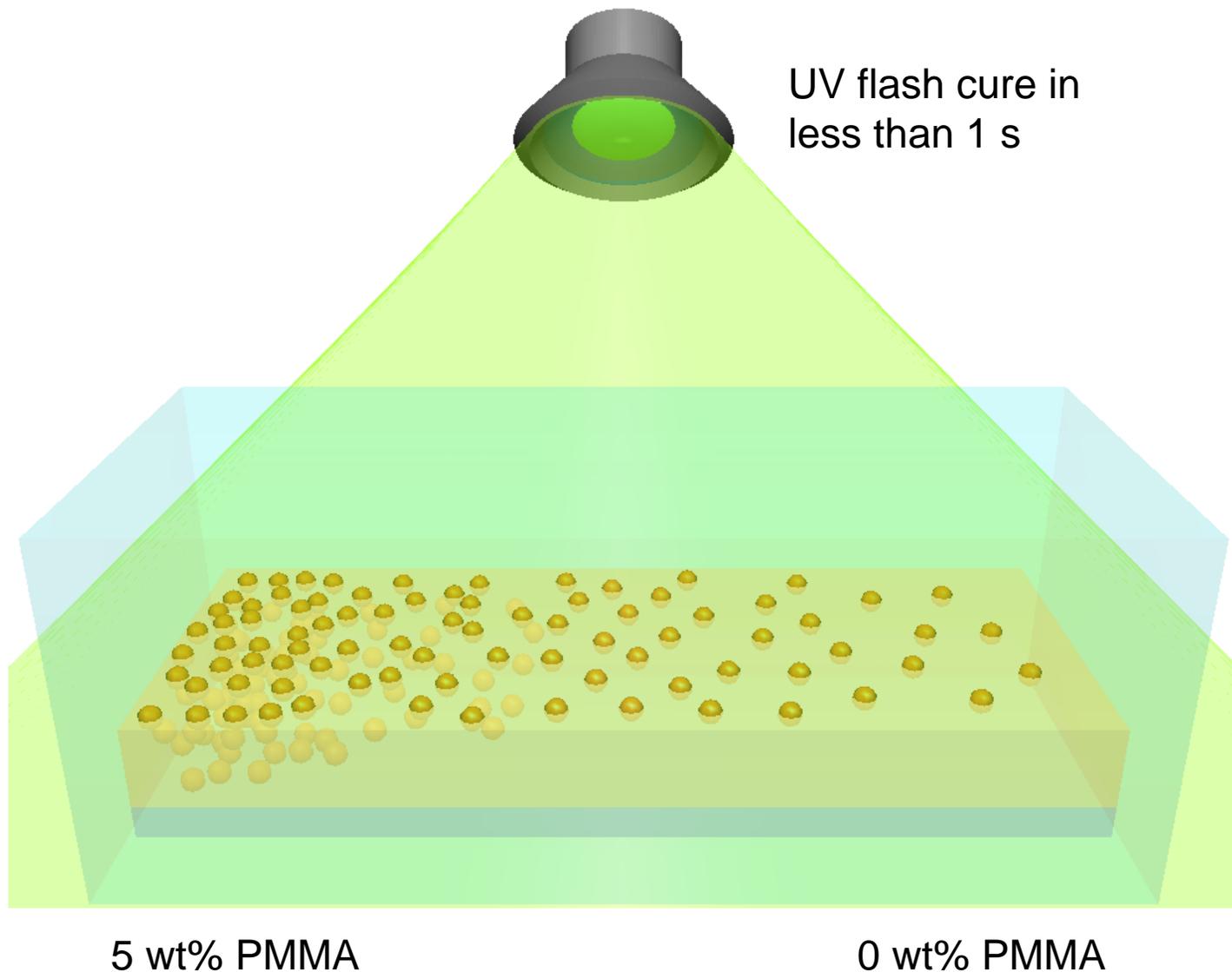
Superhydrophobic Coating



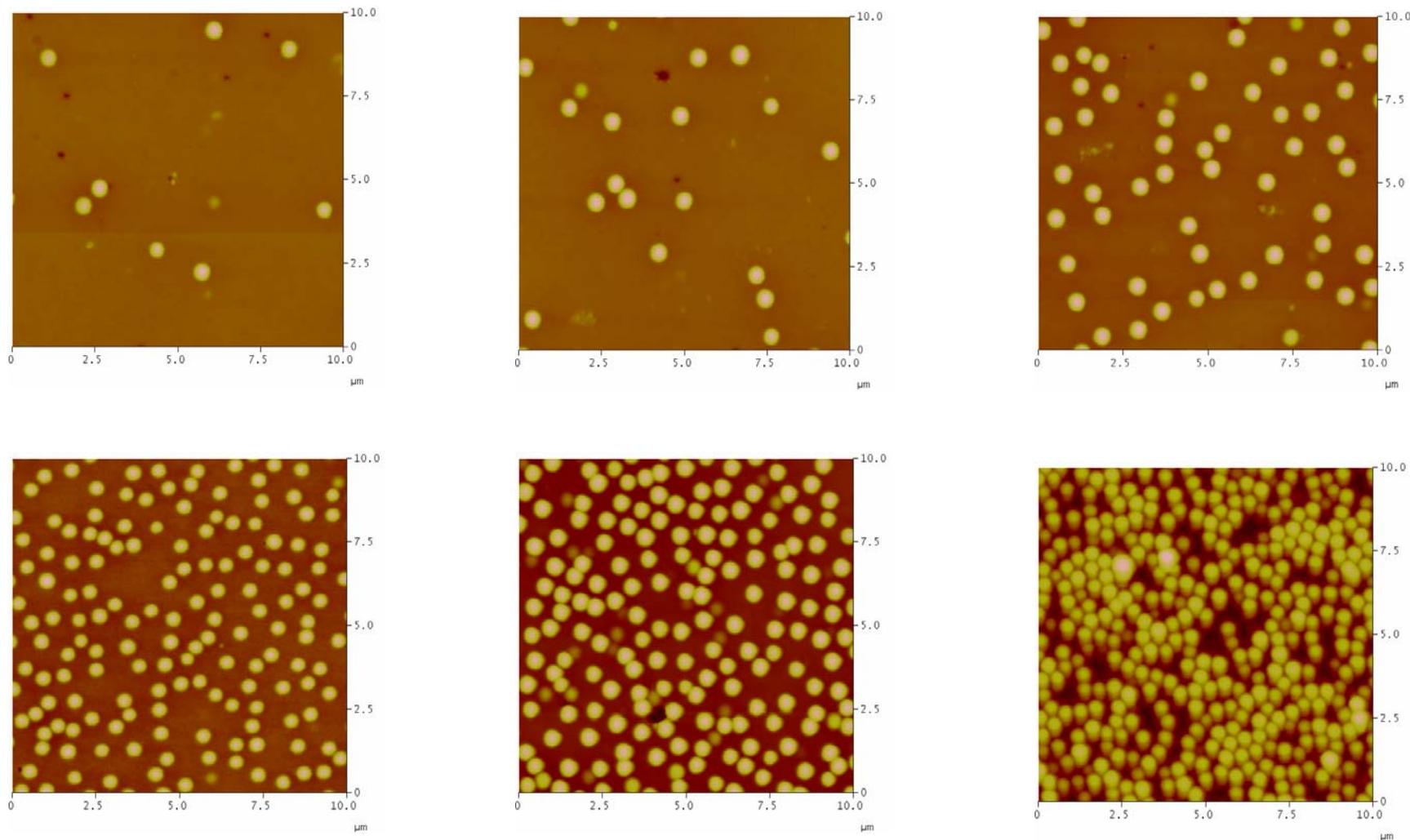
Combinatorial Approach to the Critical Wettability

Nanoparticle Coating

- Nanoparticle Segregation
 - When paint dries, the most hydrophobic material segregates to the surface
 - Most polymers are already hydrophobic
 - Many particles prefer the interior of particle
 - Dispersion is also a problem
 - Oil/Water Interface
 - Hydrophilic particles can be dispersed in water
 - Hydrophobic particles can be dispersed in oil
 - *Almost any type of particle will segregate to the oil/water interface*



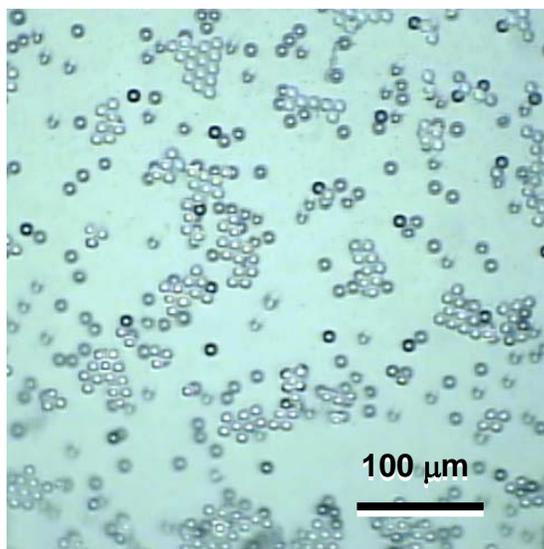
Concentration Gradient



Concentration Gradient

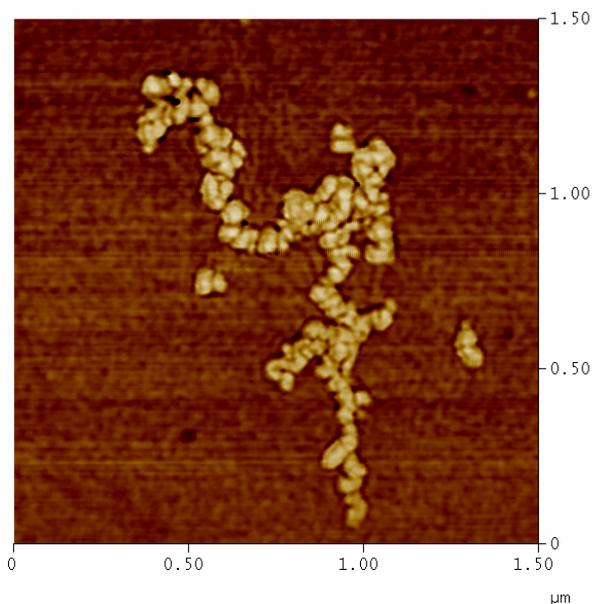
✓ Equilibrium Aggregate

soap bubbles on the surface of water



Reaction Limited Aggregate

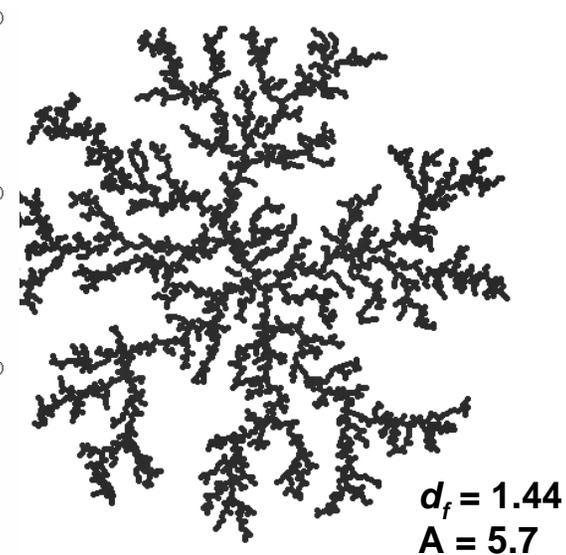
Forrest, et al. *J. Phys. A* **1979**, *12*, L109



Diffusion Limited Aggregate

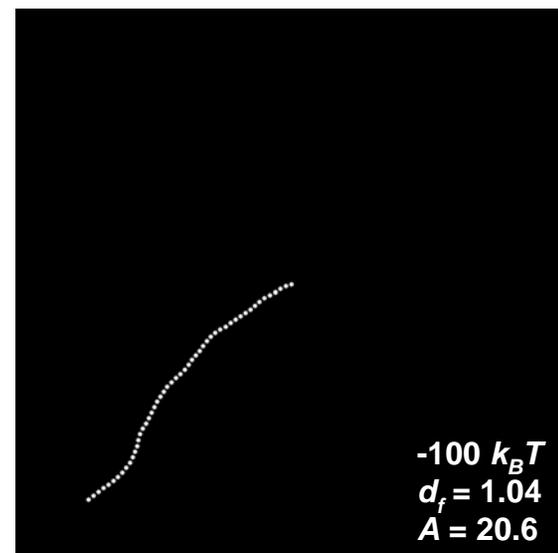
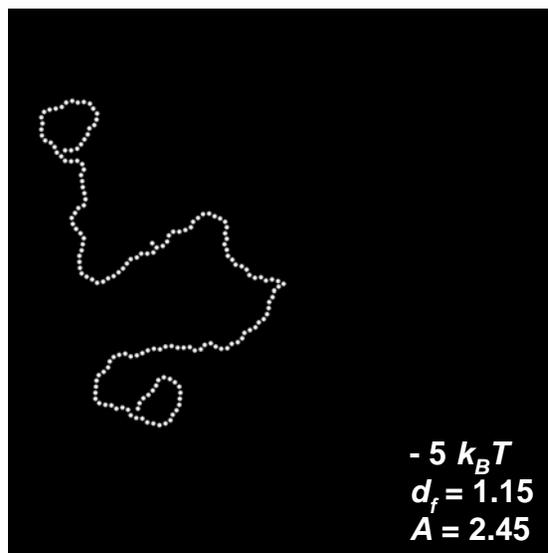
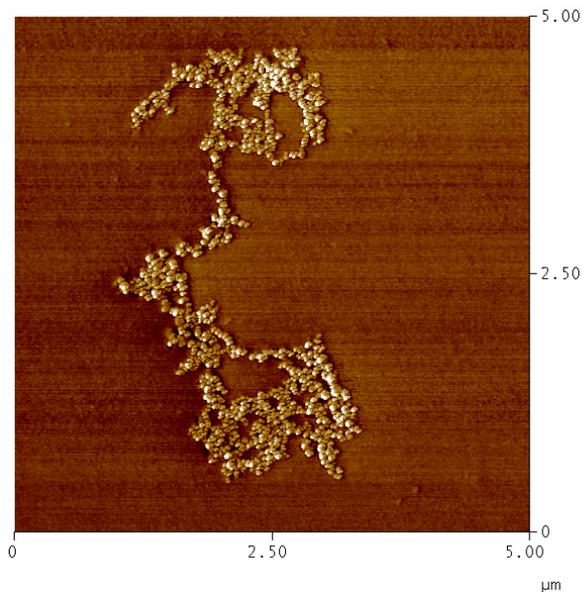
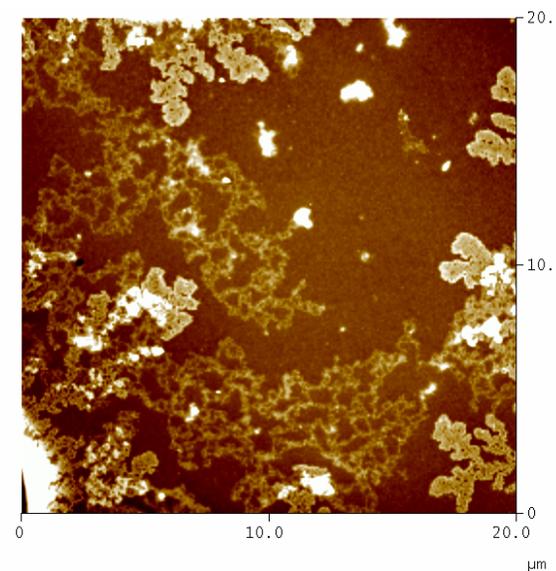
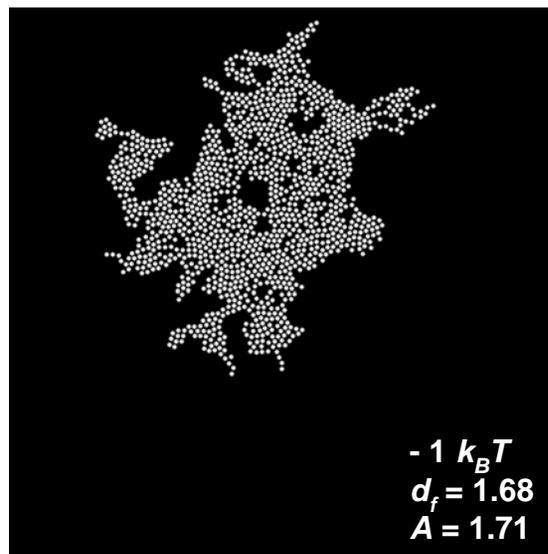
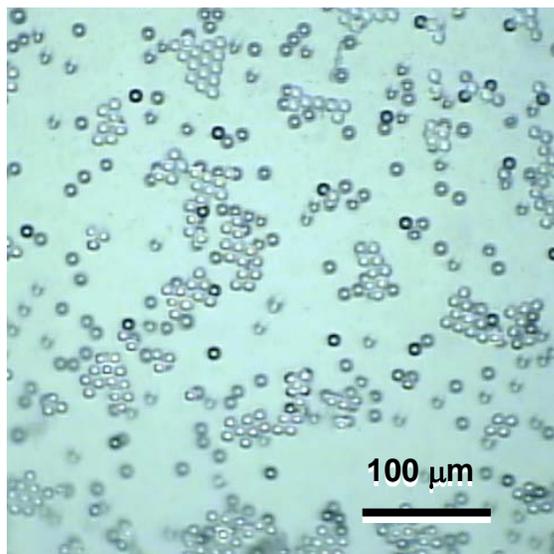
grown by Julius Su using an advanced algorithm

<http://alumnus.caltech.edu/~jsu/dla/dla.html>

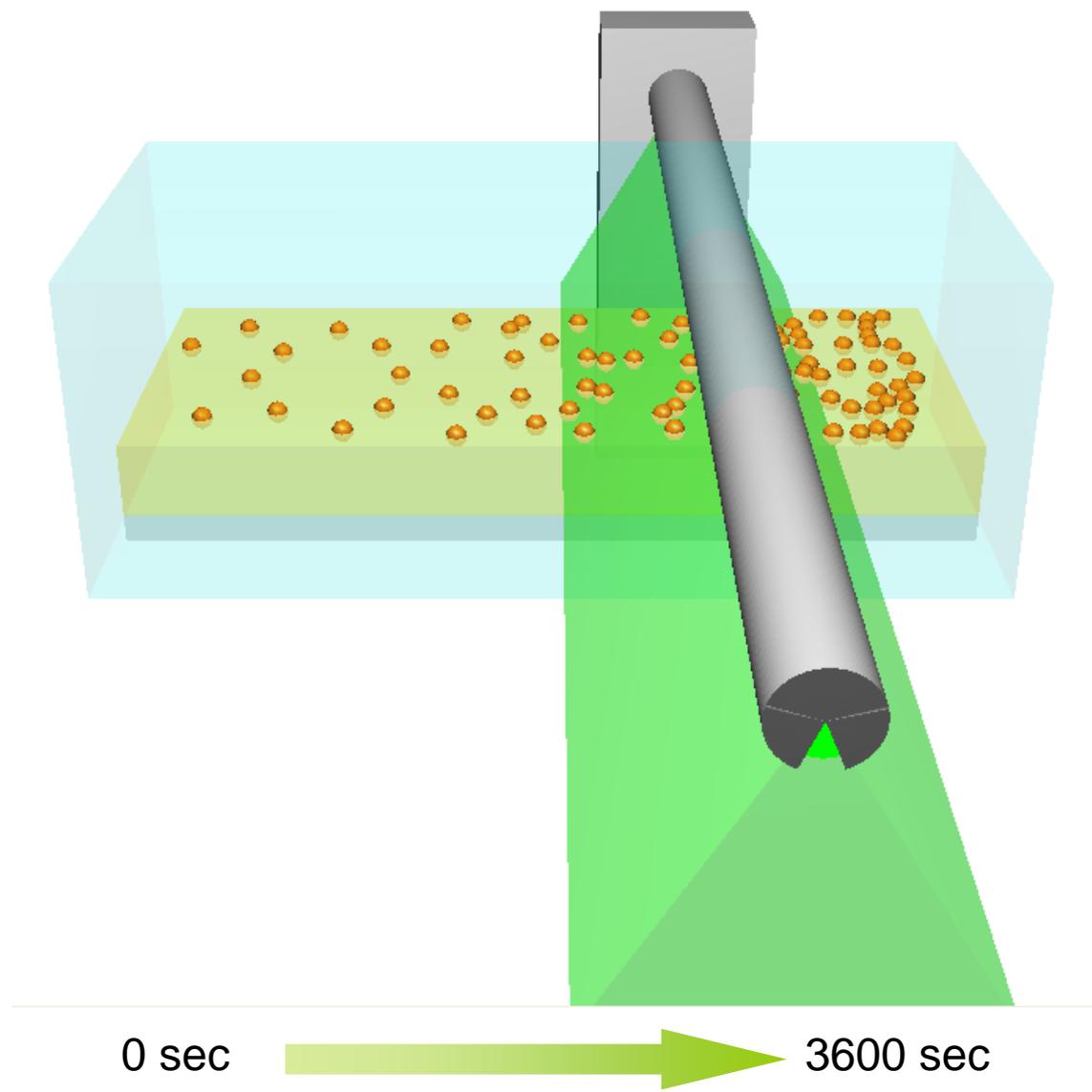


increasing binding strength

Three Aggregation Regimes



Reversible Self-Assembly

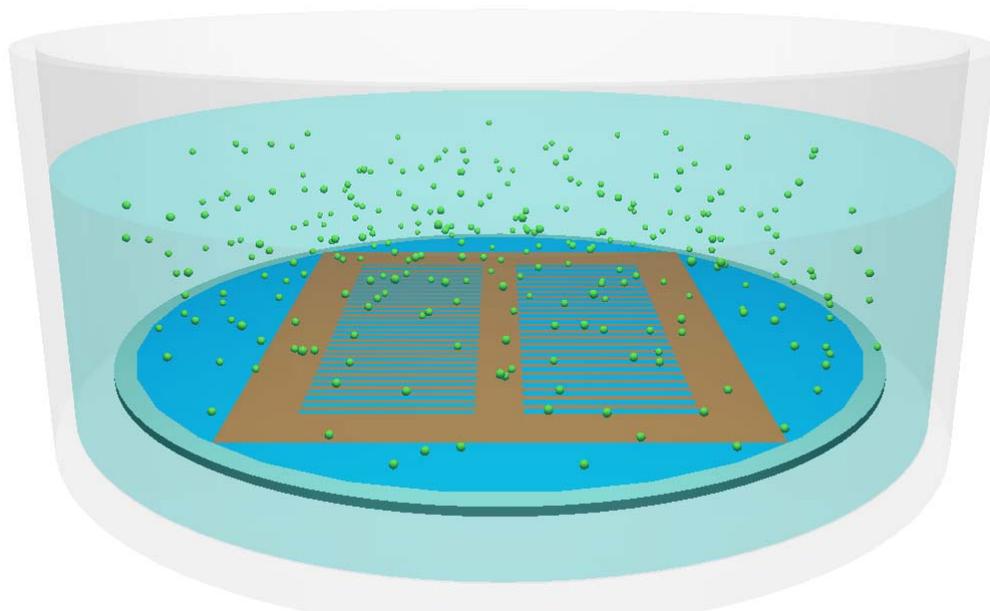


Gradient in Time

Particle/Surface Interactions

- Nanoparticle Segregation
 - Particle Deposition is a strong function of
 - Particle size
 - Surface chemistry
 - Dispersing medium (e.g. water)
 - Can measure surface properties
 - Nanoparticles can “detect” defects
 - Labeled particles can be used to identify defect locations
 - Strength of interaction is a measure of surface properties
 - *May also be able to “heal” a surface through selective deposition at defects*

- Sharp chemical contrast on surface
- Compare physical bonding with chemical bonding



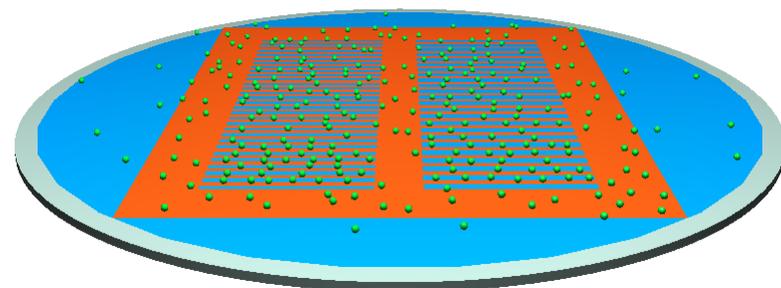
0.01% particle suspension

10 mM HEPES

100 mM NaCl

5 mM EDC

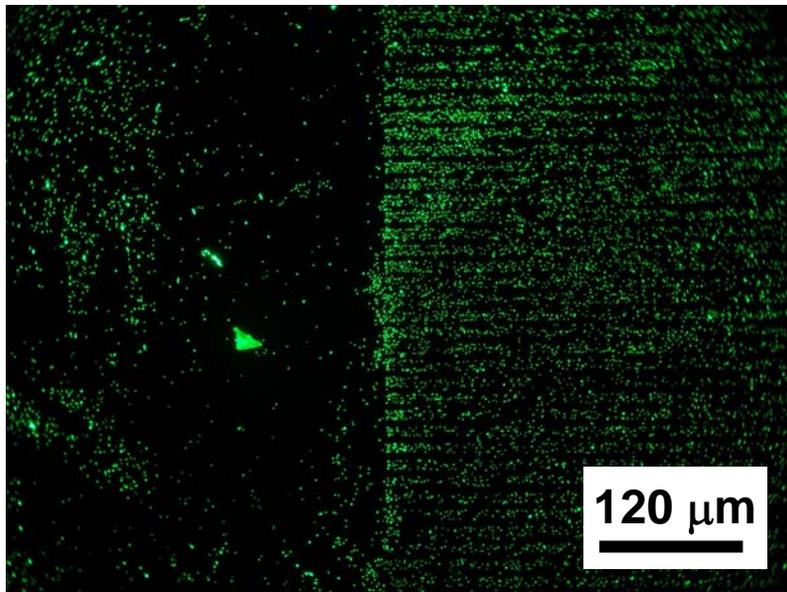
pH 8



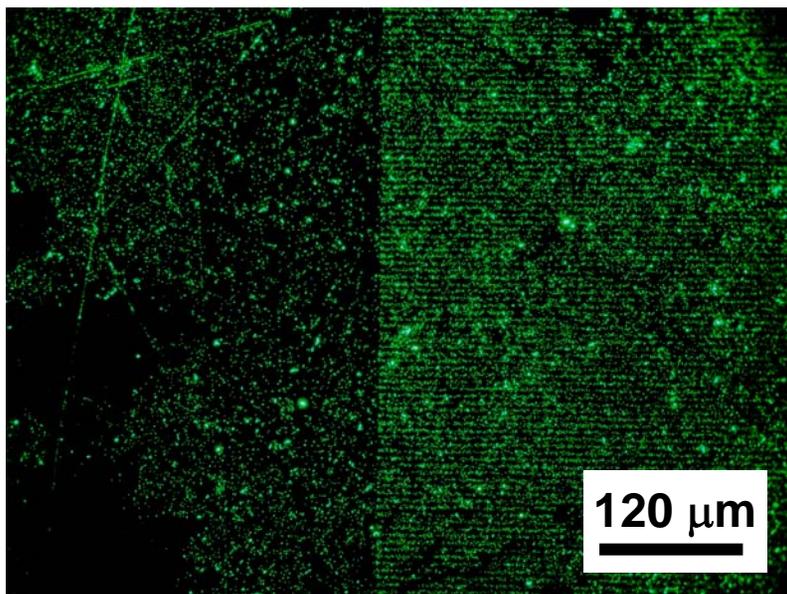
Dilute with deionized
water and dry

Particles
preferentially
deposit on COOH

Amine-Functionalized Particles + EDC
(NH₂ + COOH → CONH)

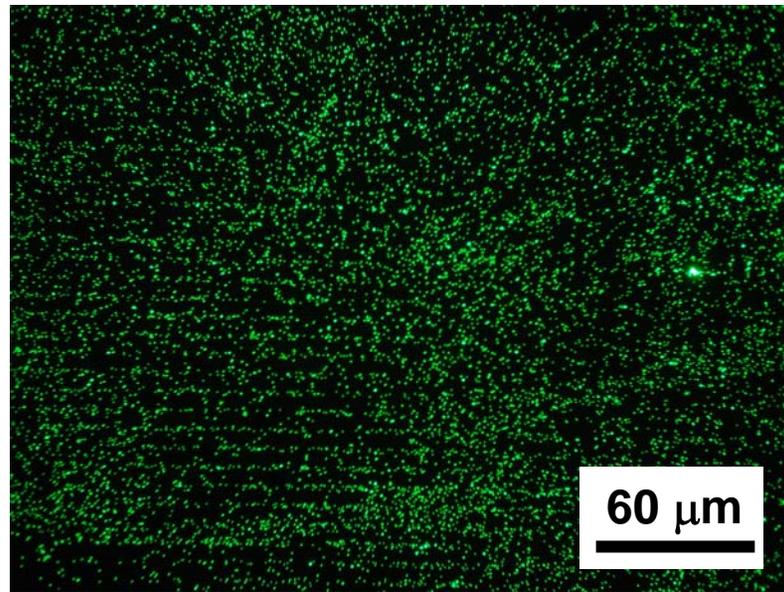


before sonication

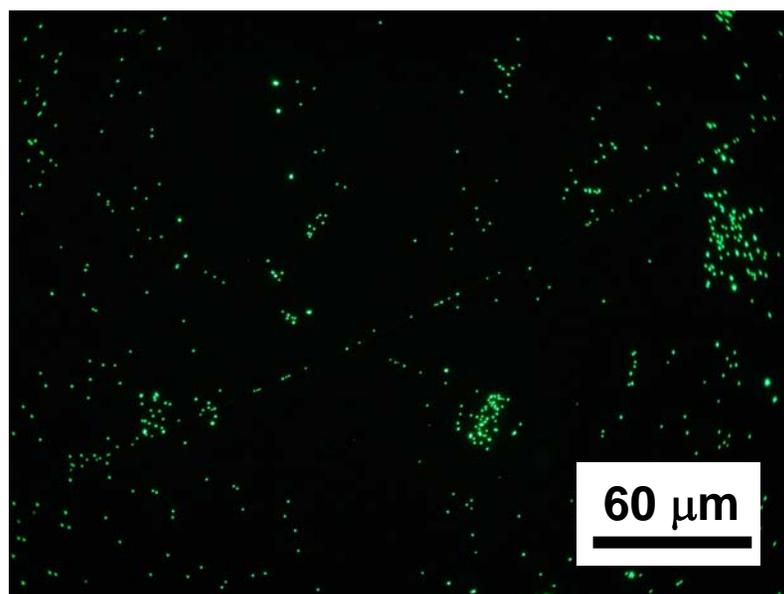


after sonication

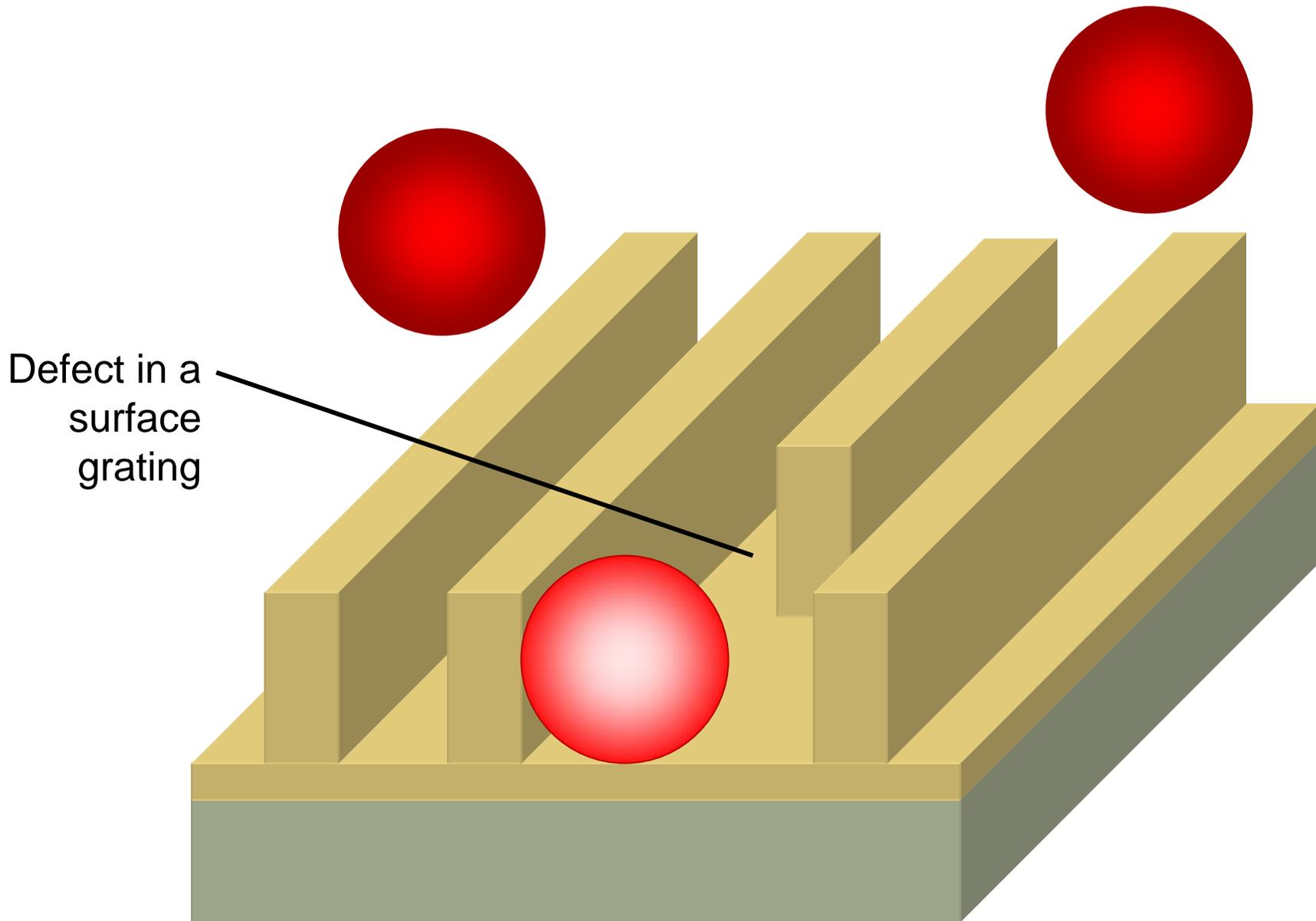
Chemical bond
Physical bond



before sonication

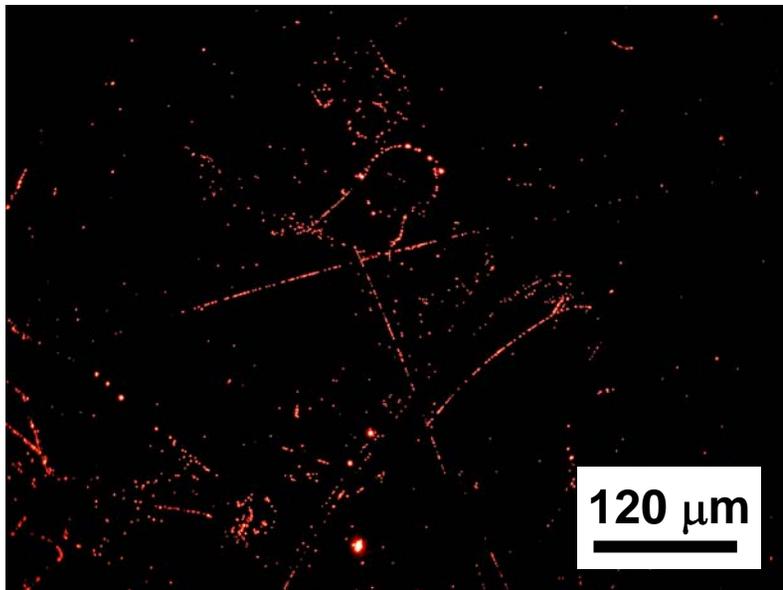


after sonication

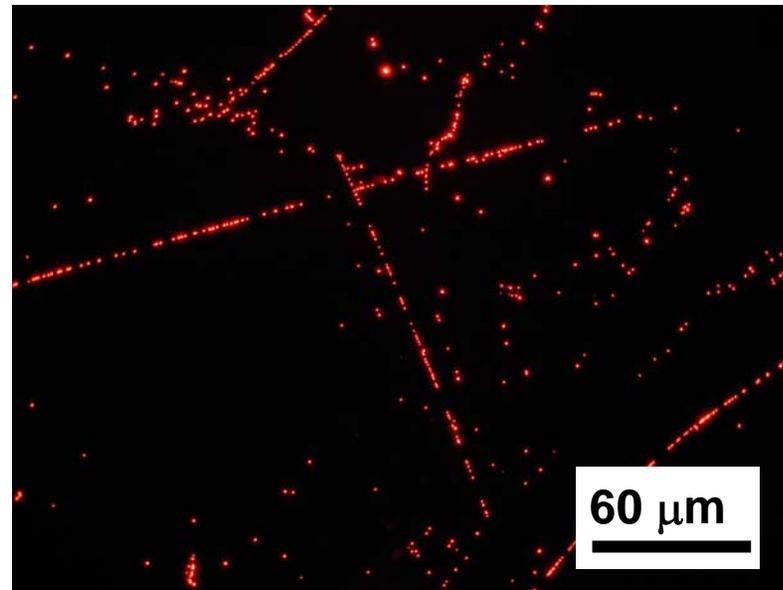


Defect in a
surface
grating

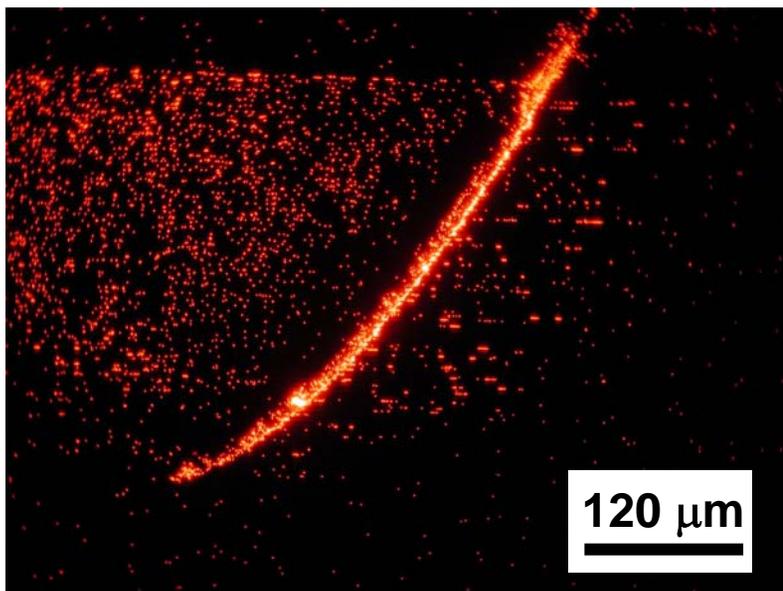
Effects of Topology



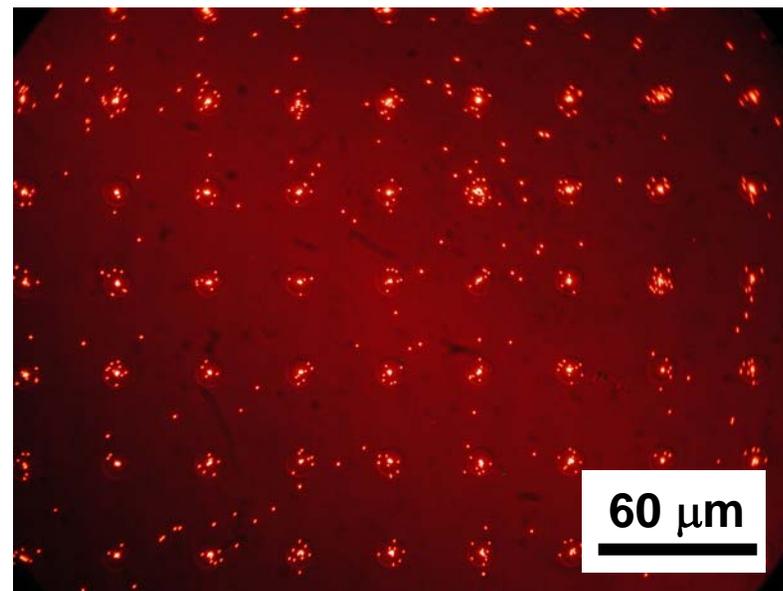
Scratches in Au film



Scratches in Au film



Scratch in Si grating



Hole Pattern in PMMA

Conclusions

- Can use “soft nanotechnology” to modify surfaces with complex structure and advanced properties
 - Colloidosomes at oil/water interface
- Model systems provide excellent starting points for the investigation of nanoparticle behavior in coatings and nanocomposites
 - Dispersion of magnetic nanoparticles in polymer coatings
- Capability to study interactions between a wide variety of particle/surface combinations
 - Particle deposition on chemical and topological surface patterns

Acknowledgements

- Jason Benkoski
- Joong Tark Han
- Matthew Becker
- Silvia Lacerda
- Brian Berry
- Ronald Jones
- Michael Fasolka
- Eric Amis