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Scalable Assembly of Patterned Ordered Functional Micelle Arrays

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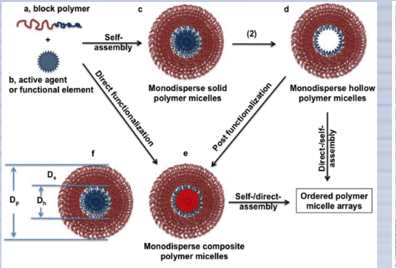
Scalable Assembly of Patterned Ordered Functional Micelle Arrays
Proposal No. 11-0940
PI: Hongyou Fan (01815), PM: William Hammetter (01815), FY10-12, Total $1.5M

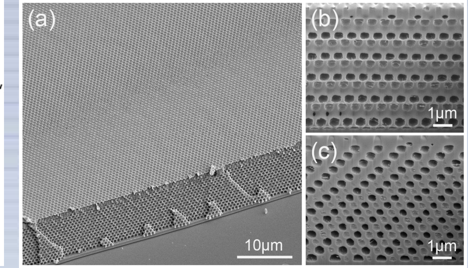
Project Purpose, Goals and Approach

Control of nanostructure in higher dimension remains an unsolved challenge. Difficulties include scalable fabrication of rapid, reliable, inexpensive patterns with large areas and multifunction in various materials systems. The goal of this proposal is to combine ordered micelle assembly with both planar and multidimensional patterning techniques for the first time, aiming to push "top-down/bottom-up" lithography into 2&3D structures and to better understand the fundamental mechanisms of nanoparticle assembly into higher dimensional structures.

Revisions to R&D Goals and Milestones

- Year 1: 1D micelle arrays on planar substrates.
- Year 2: 2D micelle arrays on 2D pattern substrates.
- Year 3: 3D micelle arrays on 3D substrates.





Key Accomplishments

- Developed a cooperative self-assembly process to synthesize monodisperse polymer micelles with narrow size distributions.
- Fabricated large area array of ordered polymer micelles.
- Fabricated 2D patterned structures.
- Performed initial work on direct assembly of polymer nanoparticles on these patterned structures.

Significance of Results

The cooperative self-assembly process for the first time enables formation of stable, monodisperse micelles/nanoparticles with the ability to precisely control size between 5-50nm with narrow size distribution and molecular length scale tunability. The method is simple and flexible for up-scale fabrications of ordered arrays.

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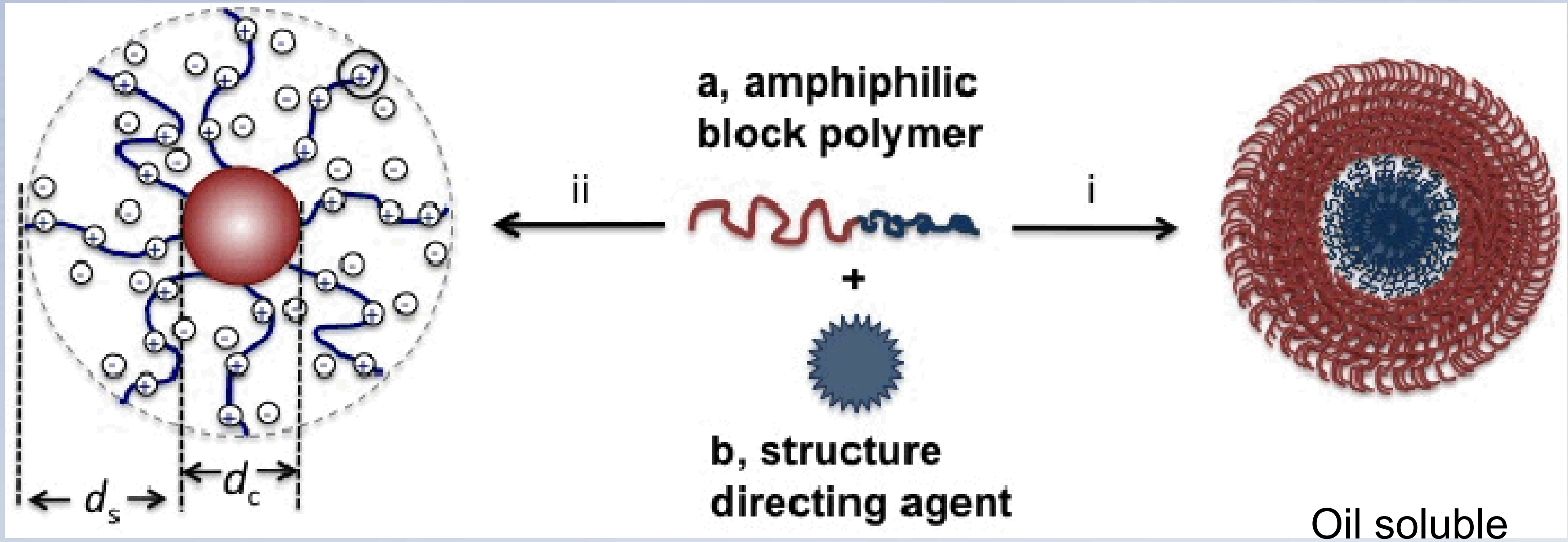
Cooperative Self-Assembly: Functional Nanoparticles Made Easy

Cooperative interactions such as hydrogen bonding, aromatic π-π stacking, charge repulsion, etc lead to block copolymer phase separation and formation of multifunctional nanoparticles with controlled size, shape, and ordered arrays.

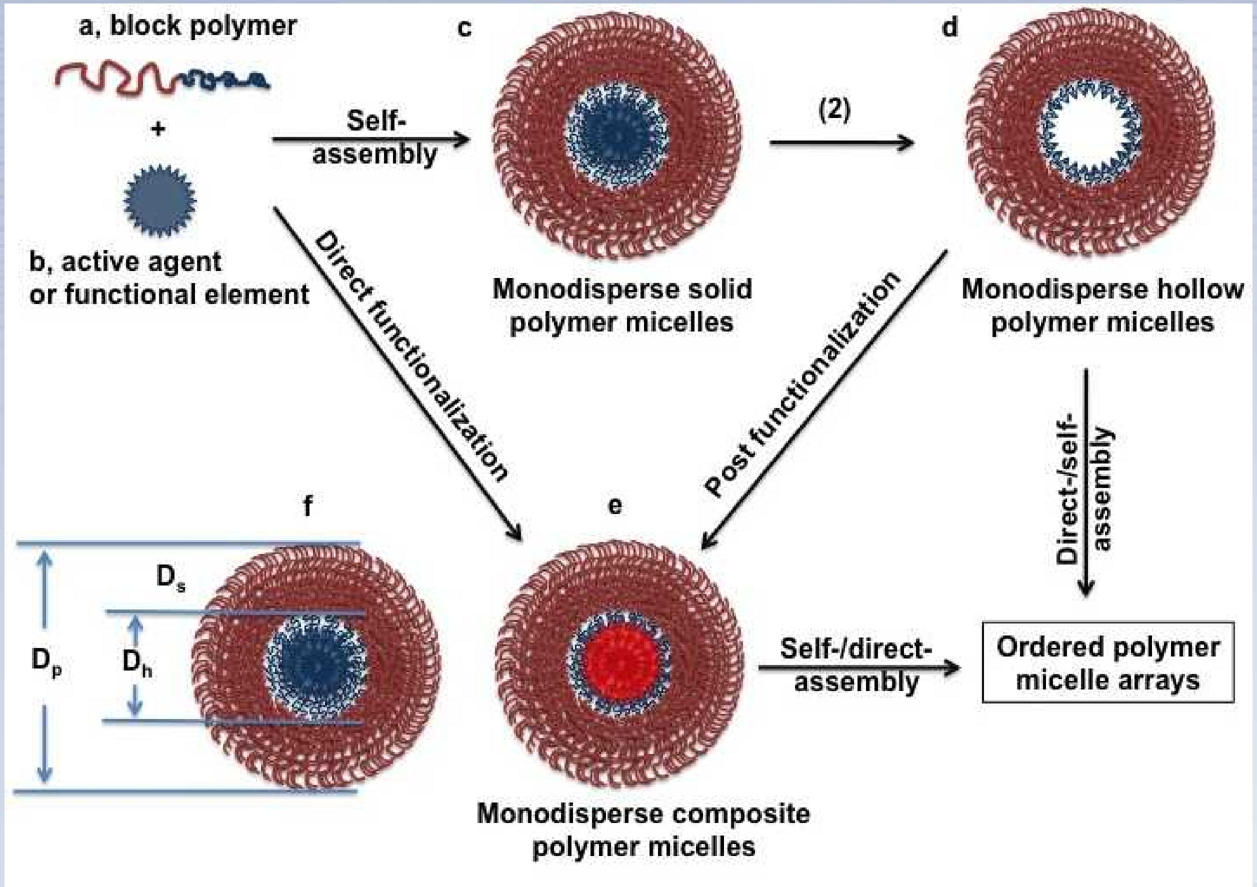


Water or alcohol soluble nanoparticles

Oil soluble nanoparticles

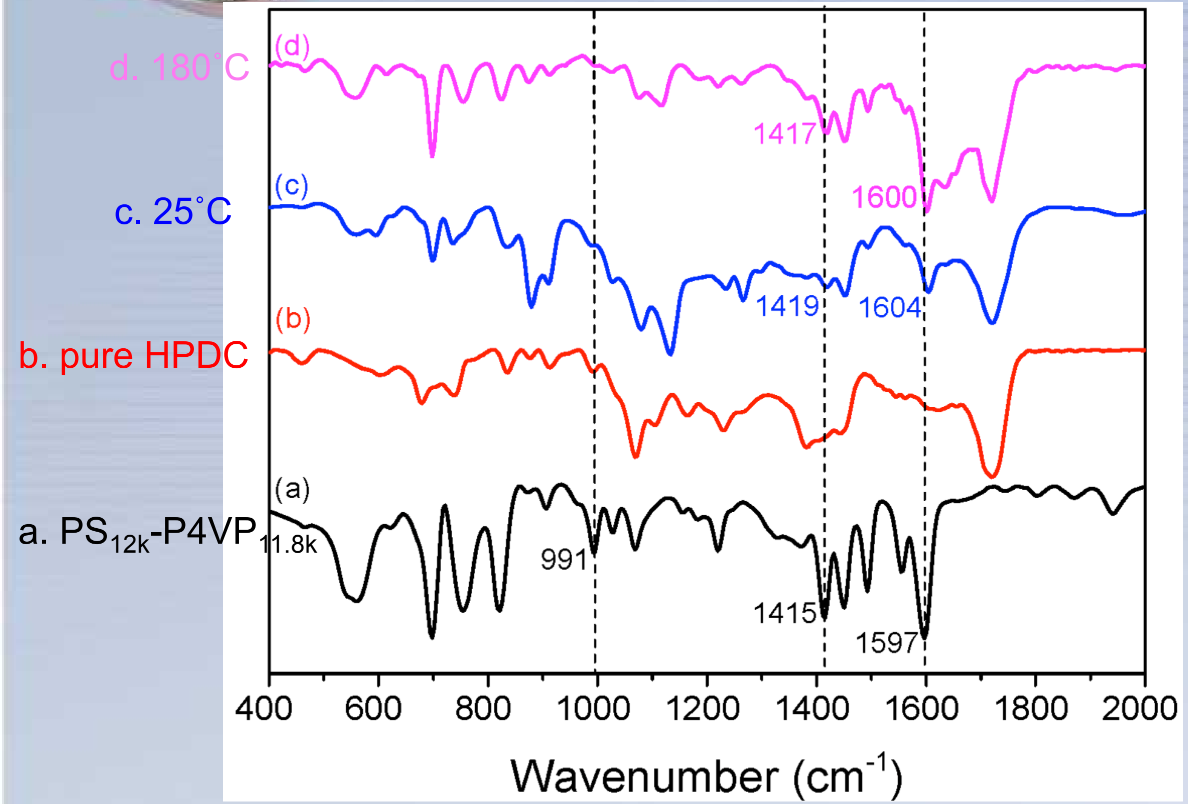
Formation of Monodisperse through Cooperative Self-Assemb

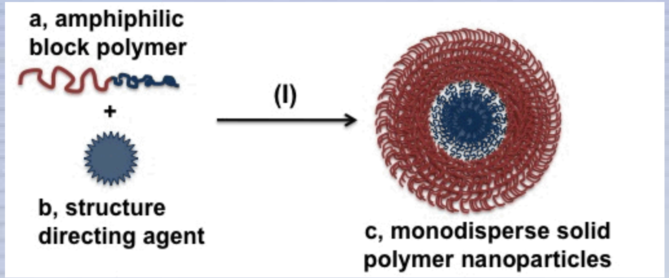
Cooperative interactions such as hydrogen bonding, aromatic π-π stacking, charge repulsion, etc lead to block copolymer phase separation and formation of multifunctional nanoparticles with controlled size, shape, and ordered arrays.

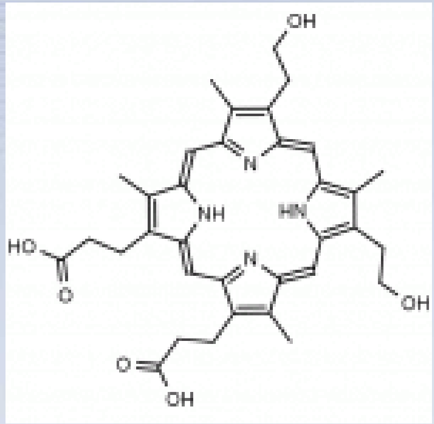


Hydrogen Bonding Driven Self-Assembly and Formation of Monodisperse Polymer Micelles

FTIR spectra







Hydrogen bonding between PVP and hydroxyl groups causes changes in the electronic distributions of the pyridine ring resulting in red-shifts for the stretching modes of the pyridine ring.

J. Y. Lee, *et al.*, *Macromolecules* **1988**, *21*, 954. A. Sidorenko, *et al.*, *J. Am. Chem. Soc.* **2003**, *125*, 12, 211.

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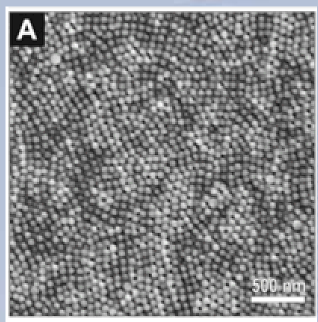
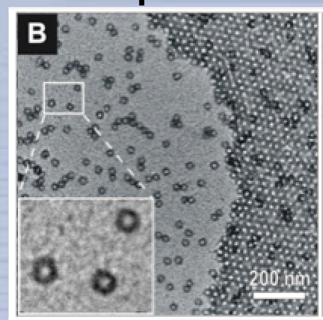
Monodisperse Polymer Nanoparticles, Nanorods

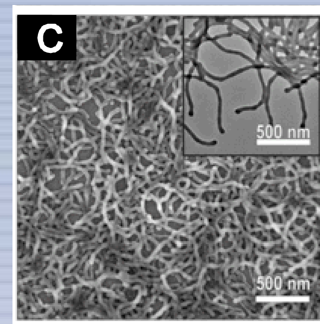
Polymer nanoparticles



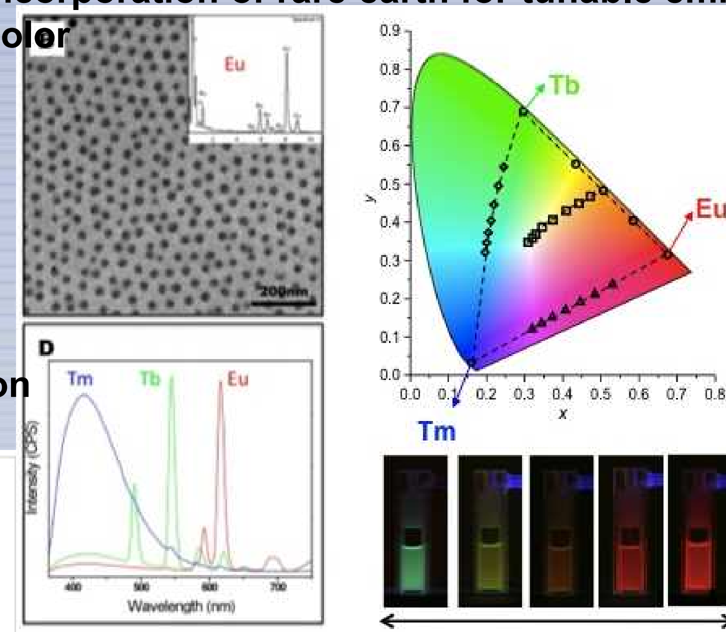
Hollow nanoparticles



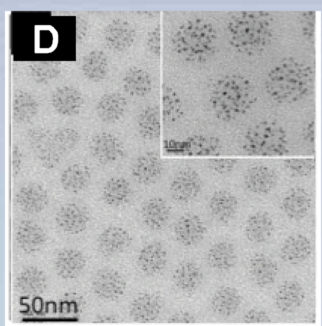
Polymer nanowires



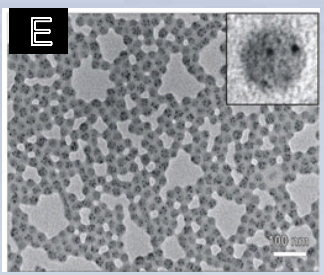
Polymer nanoparticles with controlled incorporation of rare earth for tunable emitted color



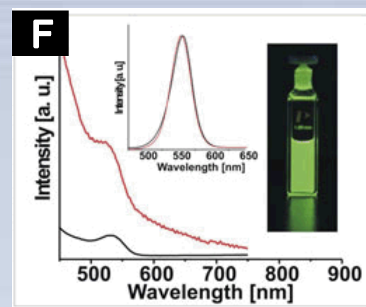
Polymer Nanoparticles/Au



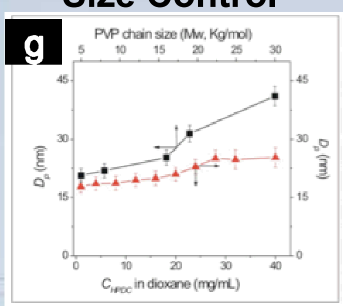
Polymer Nanoparticles/CdSe



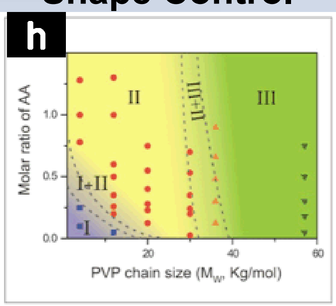
Emission/Absorption



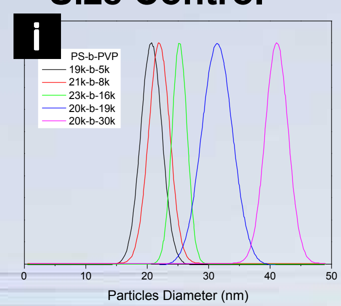
Size Control



Shape Control



Size Control



Future work:

- Continue studies of cooperative self-assembly.
- Characterize property/function.
- Explore structure-function relationship.

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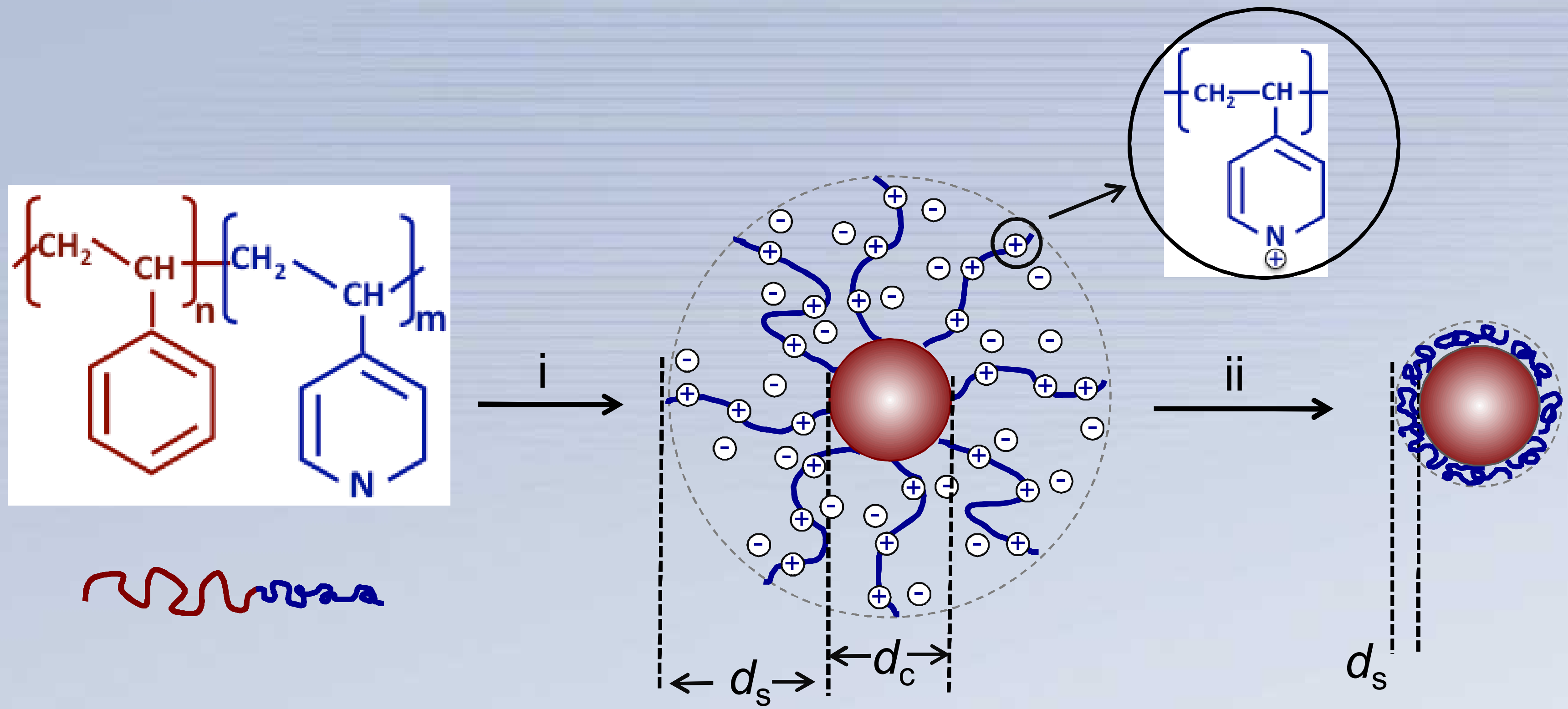
Monodisperse Water Soluble Polymer Nanopartciles through Phase Separation



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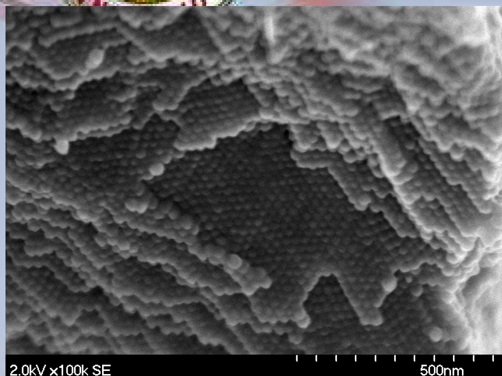
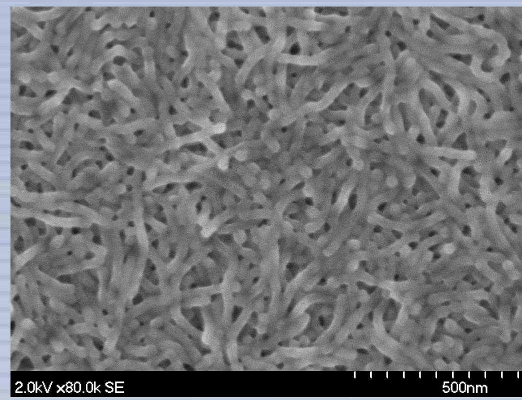
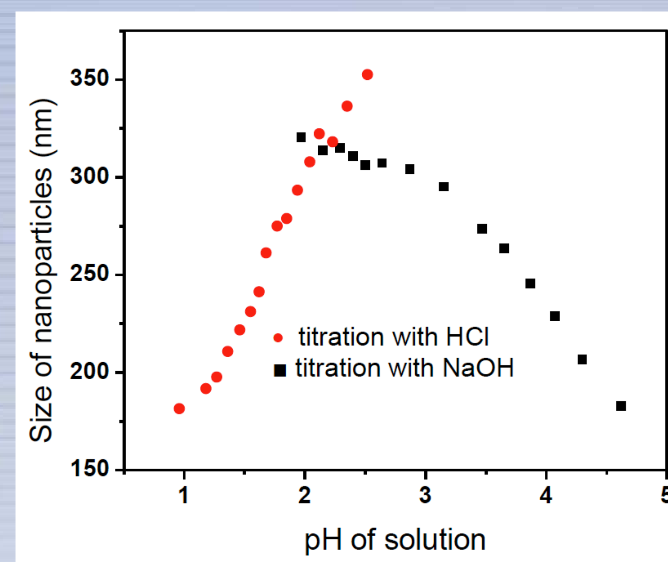
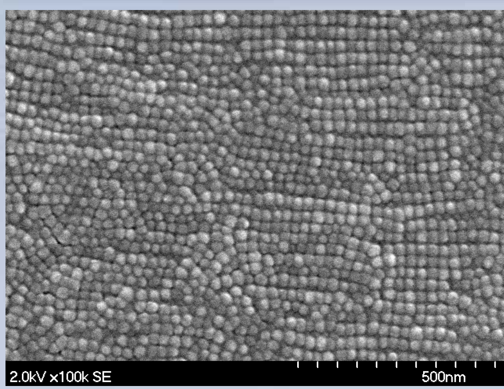
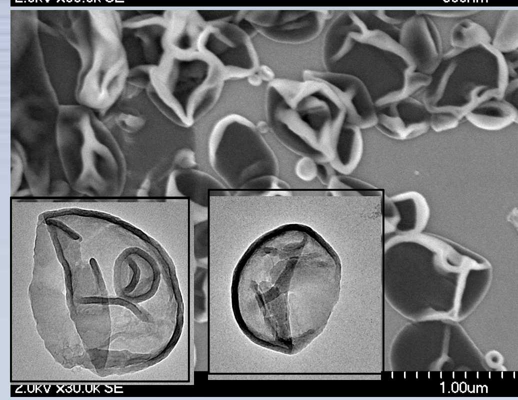
Monodisperse Water Soluble Polymer Nanoparticles with Tunable Size and Shape











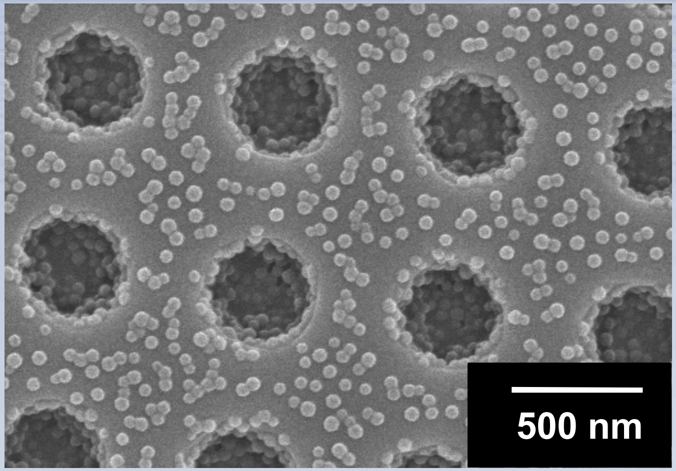
Fundamental questions:

- What is the driving force to form water-soluble nanoparticles?
- How does pH influence particle size and shape?
- What is the driving force to cause the formation of photonic crystals?
- Can we use these particles to template functional nano-composites?

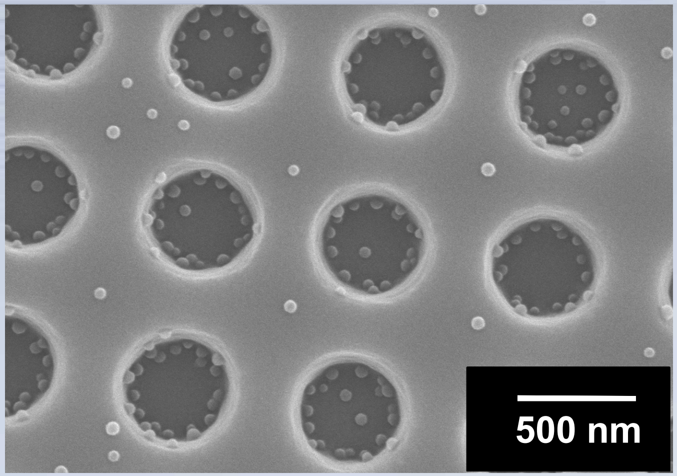
Micelle Assembly in 2D Patterns

- In a first experiment, micelles have been assembled into a simple 2D pattern created via optical holography.

High Micelle Concentration

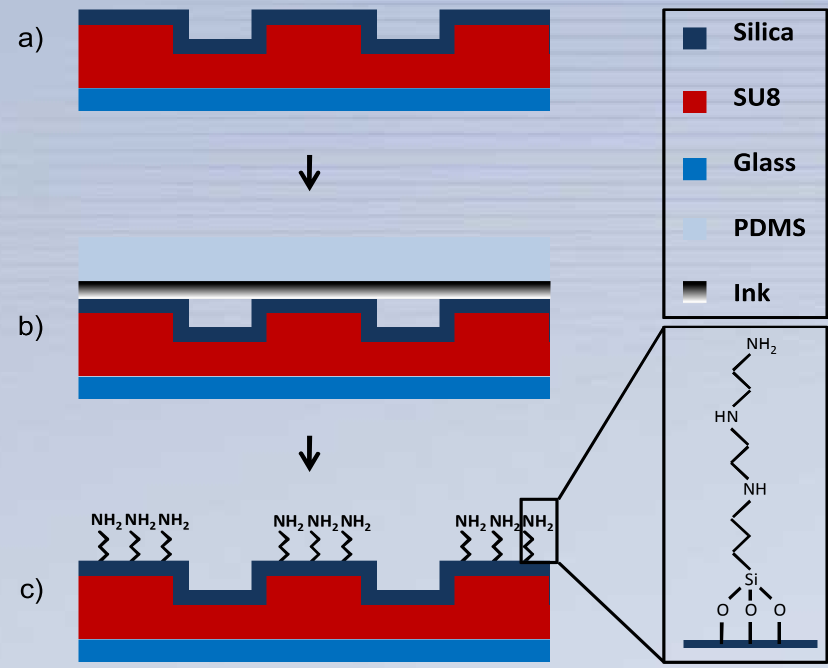


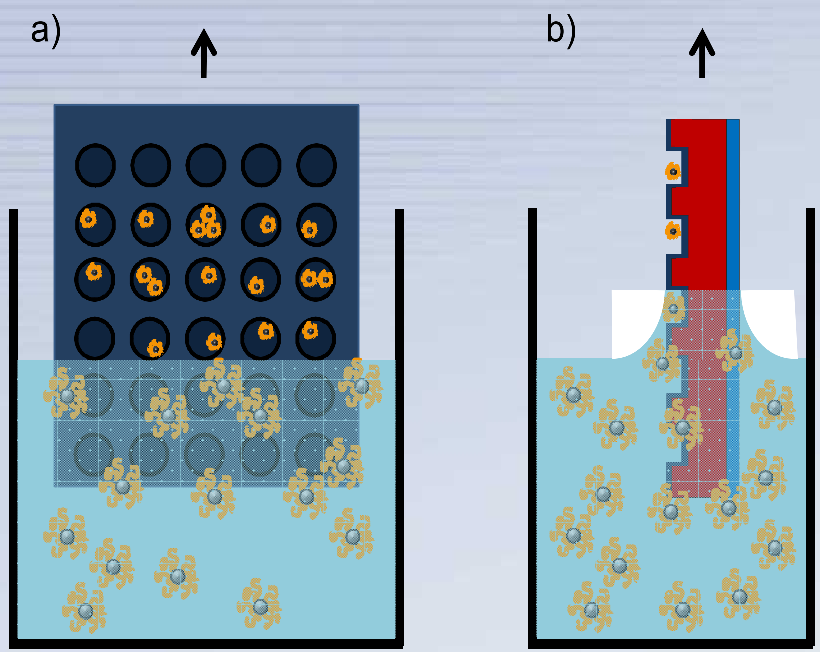
Low Micelle Concentration



- Filling of more complex structures created by nanoindentation in-progress

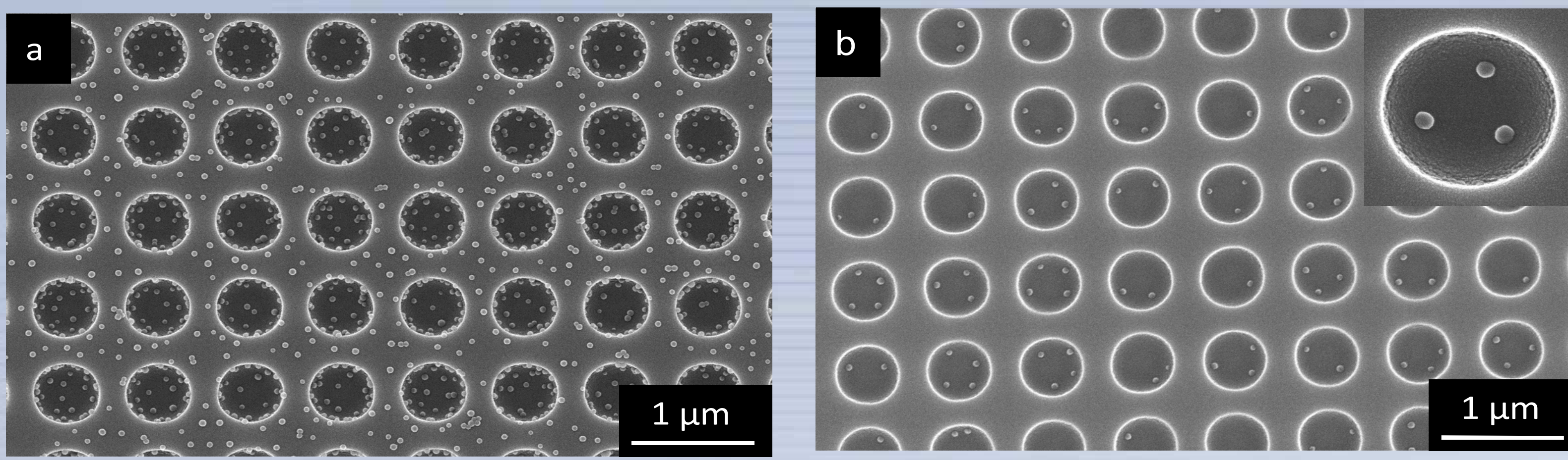
Template Directed Assembly of Dynamic Micellar Nanoparticles





Arpin, Fan, Braun, *et al*. *Soft Mater* accepted.

SEM Images of Selective Patterns

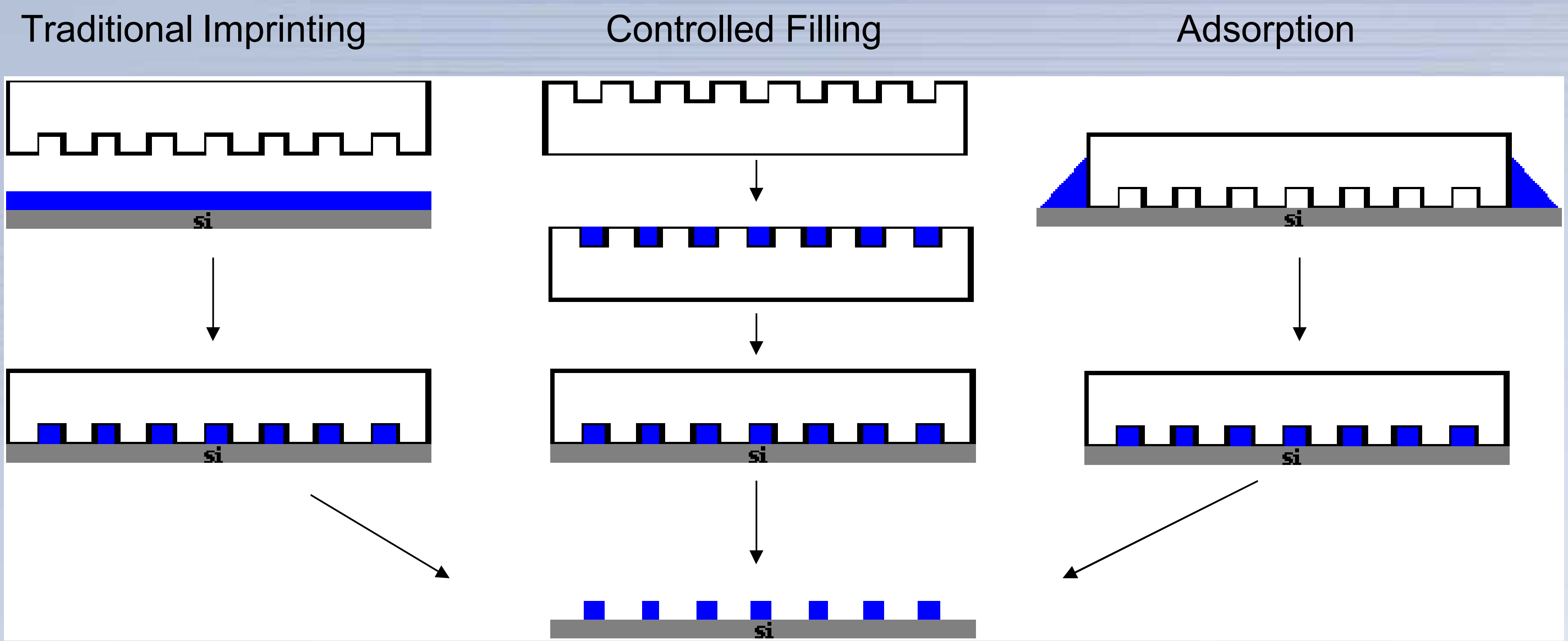


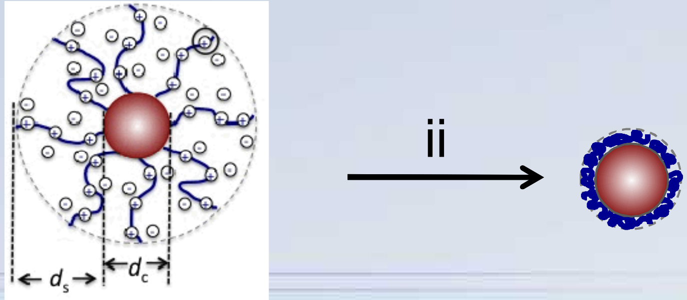
a) Template directed assembly was not observed using non-functionalized patterned substrates (no DEAS).

b) b) Representative template directed assembly of micelles using DEAS selectively functionalized patterned substrates.

Arpin, Fan, Braun, *et al*. *Soft Mater* accepted.

Imprint Lithography to Create Periodic Nanopatterns on Surfaces – Joseph Liu





Anticipated outputs/outcomes, partnerships, and scientific impacts

Anticipated Outputs and Outcomes:

Through tip-based imprinting strategies, an exceptional diversity topographic patterns can be created. Critical for many applications, the patterns formed by tip-based imprinting strategies can be registered with respect to underlying features, a very important characteristic for complex electrical and optical devices. The combination of surface and 3D patterning, in conjunction with micelles as carriers of functional objects provides the potential to create optical and electrical devices with previously unrealized functionalities.

Partnerships:

UIUC, Professors Paul Braun & Bill King and their groups & UNM

ExxonMobil & Intel

Scientific impacts:

The proposed method is a new paradigm to fabricate nanopatterns, with the ability to precisely control size between 5-50nm with molecular length scale tunability. The method is simple and flexible for up-scale fabrications. Its ability in accurate control over size, dimension (1-3D), and functionality allows fabrications of hierarchical nanostructures for deep understanding of new physics, especially in areas of plasmonic coupling, photonics, and optically based sensors.