Self-Assembly on Various Scales

Younan Xia

Department of Chemistry
University of Washintgon
Seattle, Washington 98195
E-mail: xia@chem.washington.edu

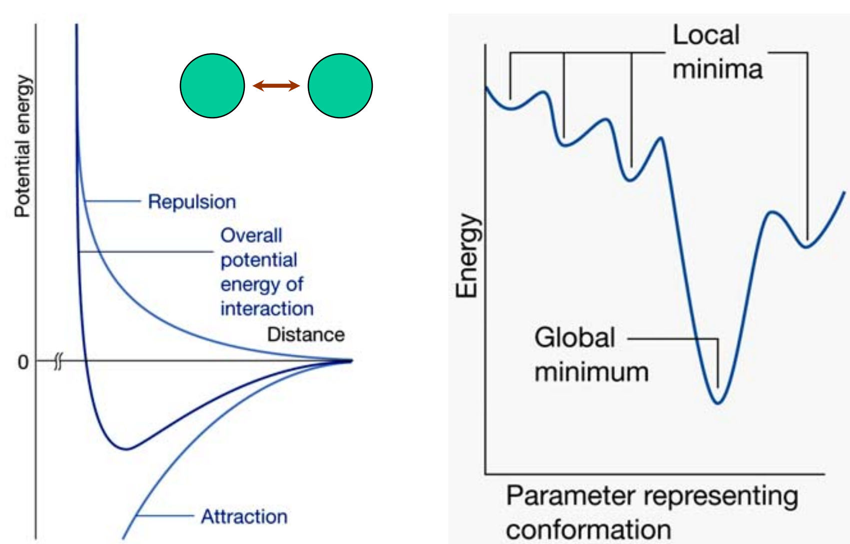
Outline

- **Self-assembly: definition, driving forces, unique features, as well as advantages**
- **Biological examples of self-assembly**
- **Chemical examples of self-assembly**
- **Nano-/Mesoscale self-assembly (MESA)**
- **Template-assisted self-assembly (TASA)**

Definition of Self-Assembly

- **<u>Self-Assembly</u> (SA) is the spontaneous organization of molecules or objects into well-defined aggregates via noncovalent interactions (or forces)**
- **<u>Building Blocks</u>: molecules and objects with *coded information* for self-assembly**
- **<u>Processing</u>: mix, shake, and form product**

Driving Forces: Attractive vs. Repulsive



Atkins & de Paula, Phys. Chem., 7th ed., Freeman, p. 705 (2002)

Driving Forces on Various Scales

- **<u>Molecular Scale</u>: H-bonding, hydrophoic interaction, electrostatic forces, "lock-key" type interactions, and van der Waals forces**

- **<u>Nano- and Mesoscale</u>: capillary forces, external fields (gravitational, centrifugal, magnetic, electric, optical, ……), surface tension, electrostatic forces, shear forces, and molecule-based interactions**

Attractive Features of Self-Assembly

- **Self-assembly proceeds spontaneously**

- **The self-assembled structure is often at or close to thermodynamic equilibrium**

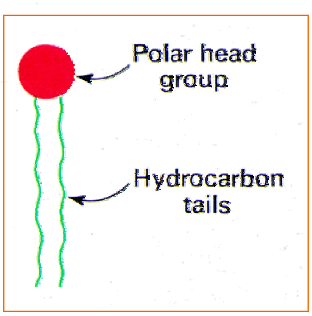
- **Self-assembly tends to reject defects, and also has self-healing capability**

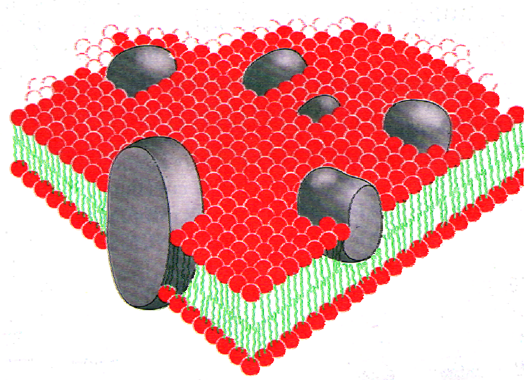
- **The self-assembled structure often has greater order than other systems do (free energy: entropy vs. enthalpy)**

What Might Self-Assembly Bring to Us?

- Simple, parallel, low-cost processing
- Small and/or multifuctional structures
- Complex structures with fewer defects
- Repetitive or reconfigurable structures
- Fabrication in inaccessible spaces

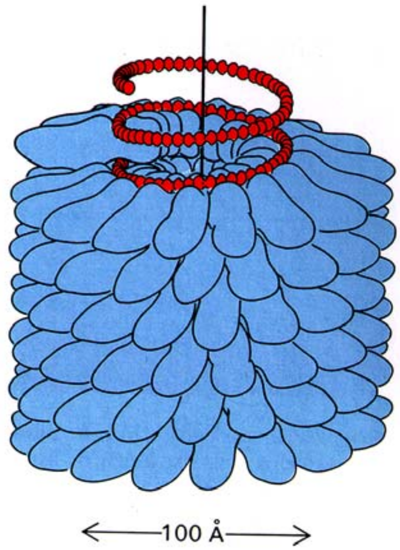
Lipid Molecules and Cell Membranes





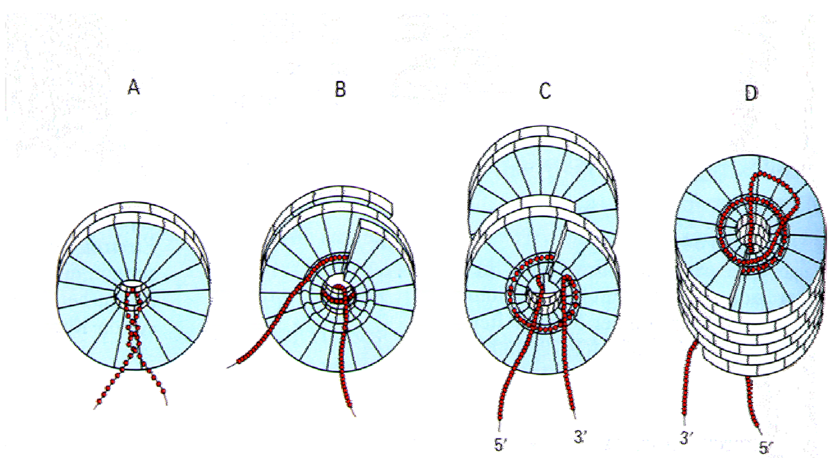
Stryer, Biochemistry, 3rd ed., W. H. Freeman, 1988, p.296

Tobacco Mosaic Virus (TMV)



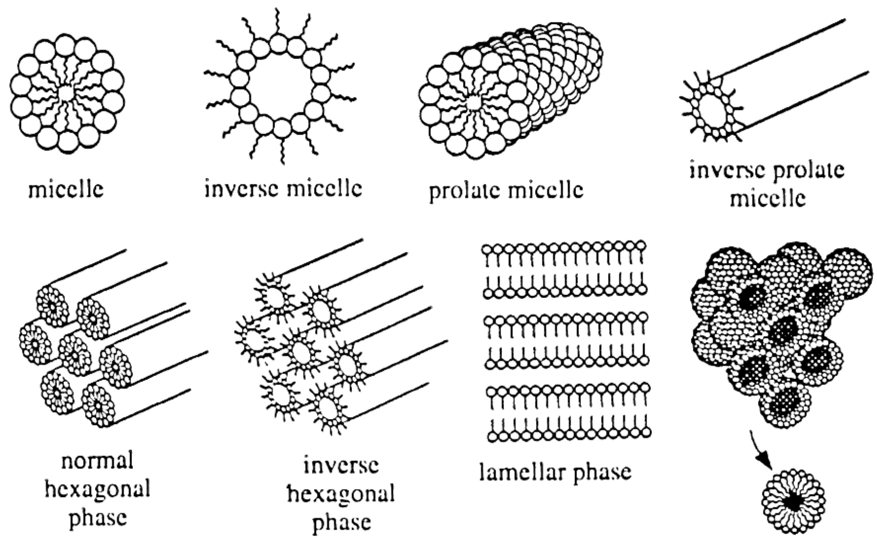
Stryer, Biochemistry, 3rd ed., W. H. Freeman, 1988, p.852

How Does TMV Self-Assemble?

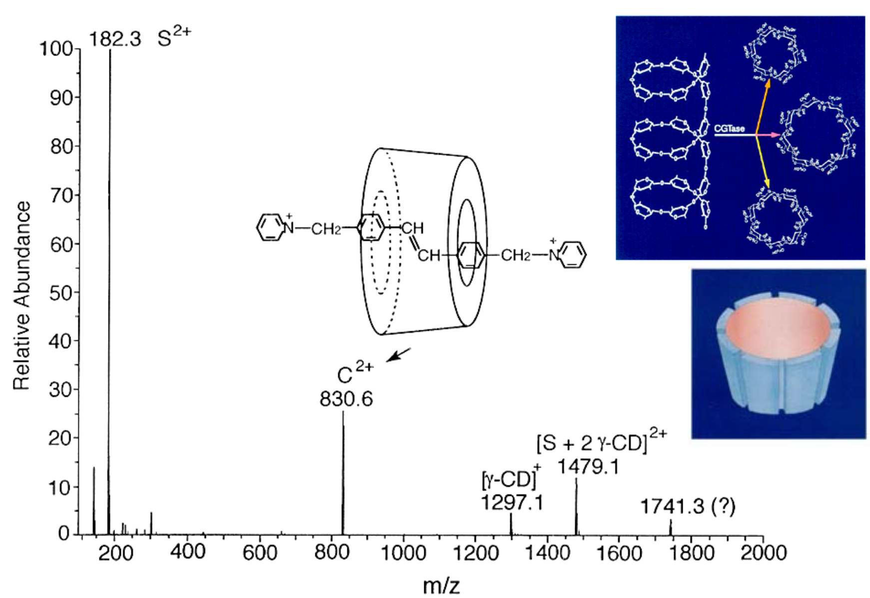


Stryer, Biochemistry, 3rd ed., W. H. Freeman, 1988, p.854

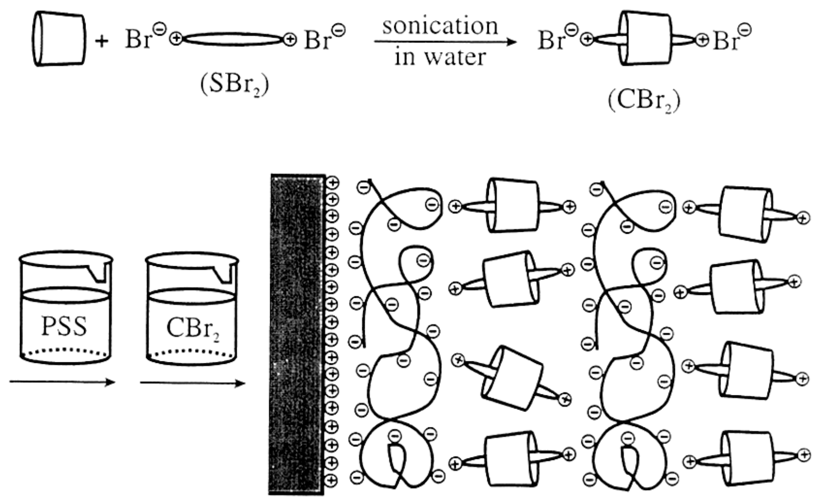
Self-Assembly of Surfactant (Soap) Molecules



Self-Assembly via Hydrophobic Interaction

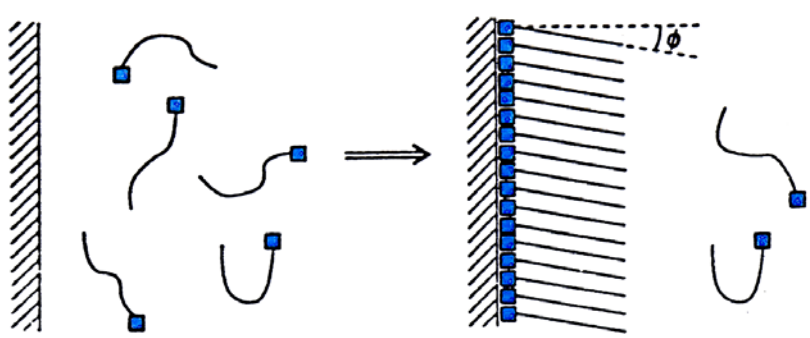


Self-Assembly via Electrostatic Interactions



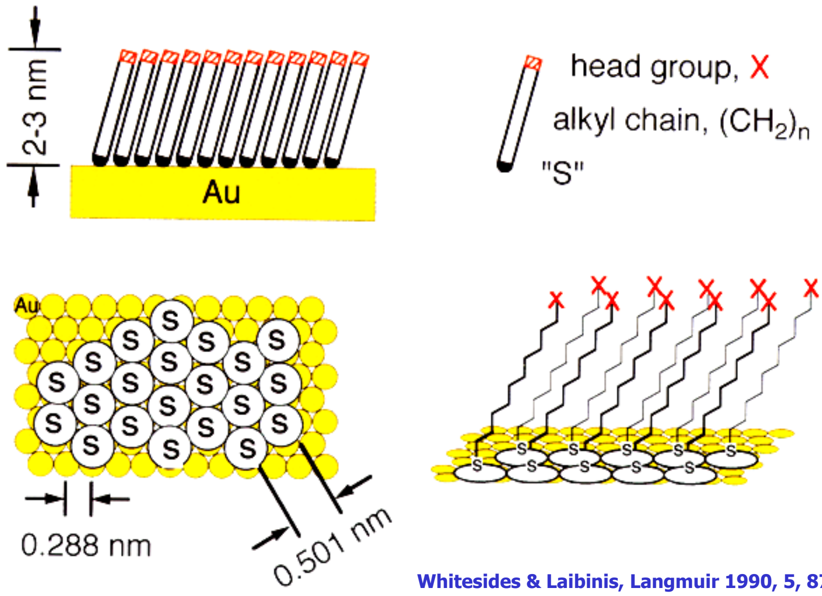
Dreja, Kim, Yin & Xia, Journal of Materials Chemistry 2000, 10, 603

Self-Assembled Monolayers (SAMs)



Bain & Whitesides, Advanced Materials 1989, 4, 506

Alkanethiolate SAMs on Gold Surfaces



Whitesides & Laibinis, Langmuir 1990, 5, 87

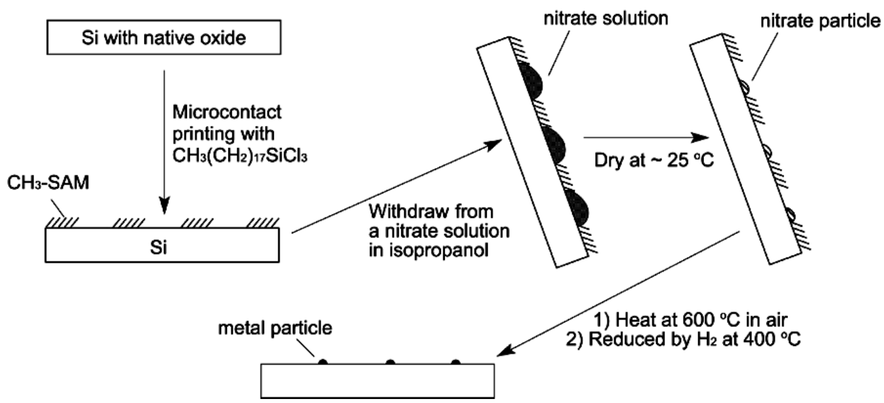
Substrate and Ligand Pairs for Forming SAMs

Substrate	Ligand or Precursor	Binding
Au	RSH, ArSH (thiols)	RS-Au
Au	RSSR' (disulfides)	RS-Au
Au	RSR' (sulfides)	RS-Au
Au	RSO_2H	RSO_2-Au
Au	R_3P	R_3P-Au
Ag	RSH, ArSH	RS-Ag
Cu	RSH, ArSH	RS-Cu
Pd	RSH, ArSH	RS-Pd
Pt	RNC	RNC-Pt
GaAs	RSH	RS-GaAs

Substrate	Ligand or Precursor	Binding
InP	RSH	RS-InP
SiO_2, glass	$RSiCl_3$, $RSi(OR')_3$	siloxane
Si/Si-H	$(RCOO)_2$ (neat)	R-Si
Si/Si-H	$RCH{=}CH_2$	RCH_2CH_2Si
Si/Si-Cl	RLi, R-MgX	R-Si
metal oxides	RCOOH	$RCOO^- \cdots MO_n$
metal oxides	RCONHOH	$RCONHOH \cdots MO_n$
ZrO_2	RPO_3H_2	$RPO_3^{2-} \cdots Zr(IV)$
In_2O_3/SnO_2 (ITO)	RPO_3H_2	$RPO_3^{2-} \cdots M(n+)$

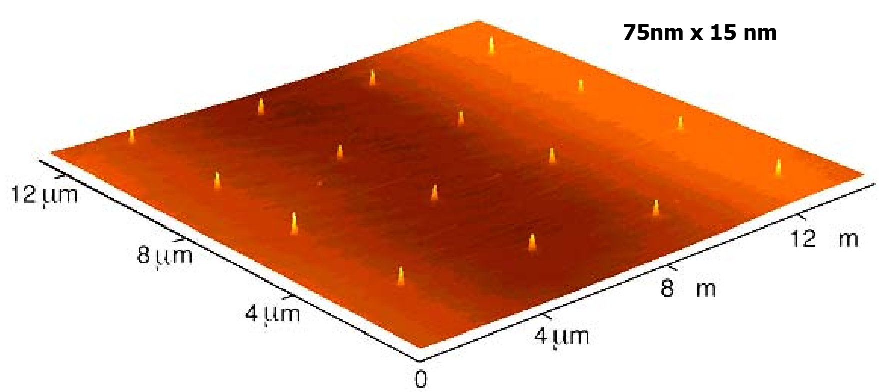
Xia & Whitesides, Angew. Chem. Int. Ed. Engl. 1998, 37, 550

Fabrication of Arrayed Magnetic Nanoparticles

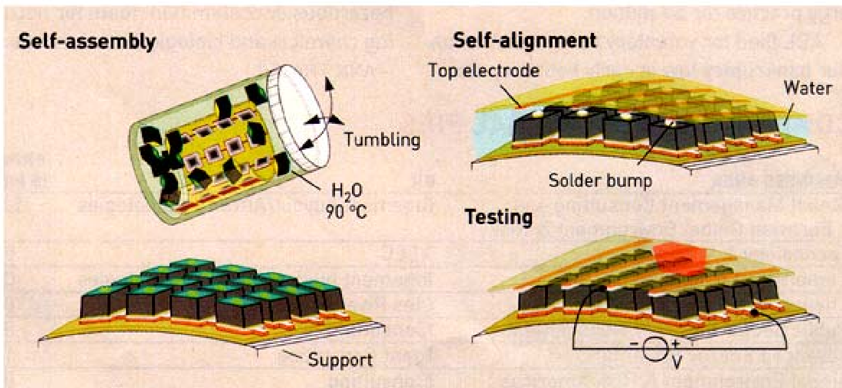


Zhong, Gates, Xia & Qin, Langmuir, 2000, 16, 10369

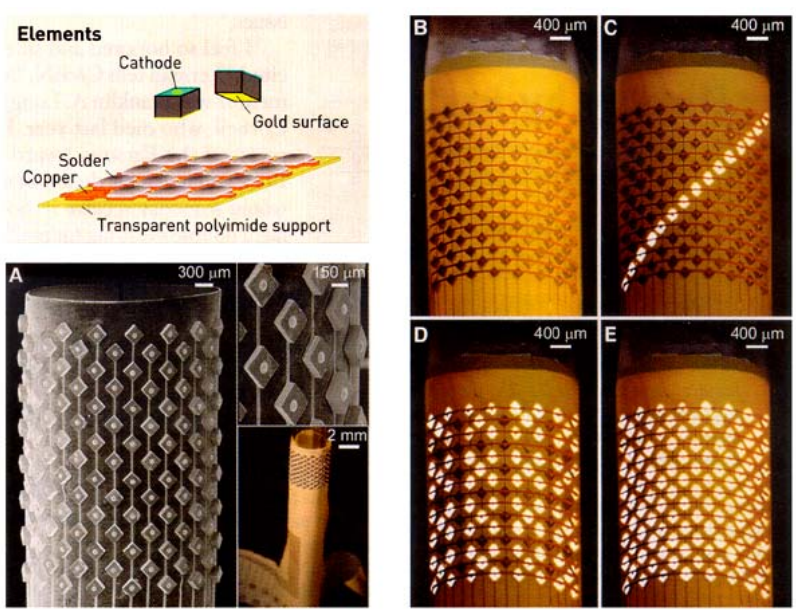
Arrayed Co Nanoparticles on SiO_2/Si Substrate



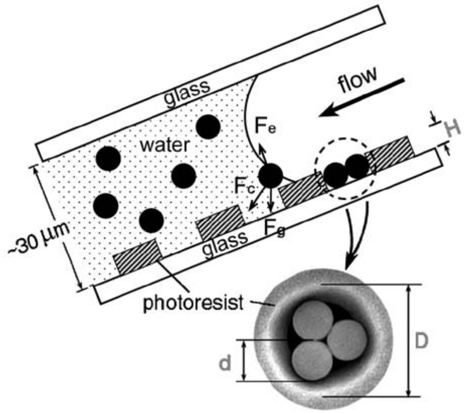
Fabrication of Arrayed LEDs by Self-Assembly

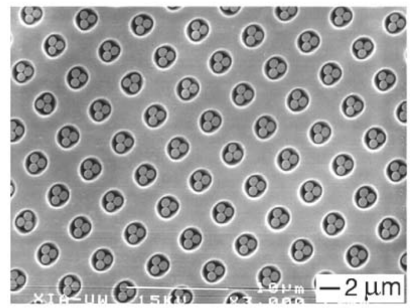


Whitesides et al, Science, 2002, 296, 323



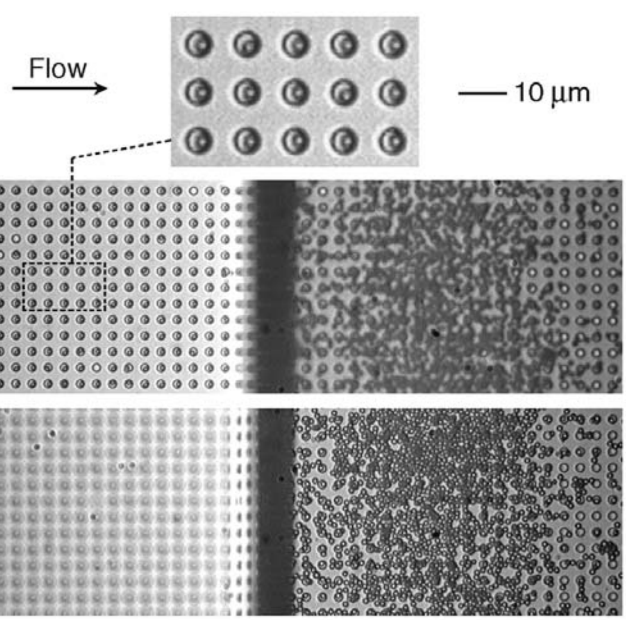
Template-Assisted Self-Assembly (TASA)



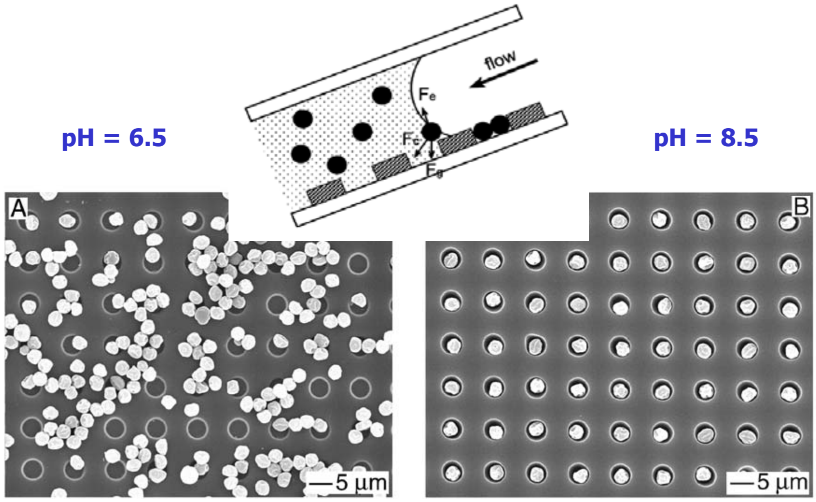


Yin & Xia, Advaced Materials 2001, 13, 267
Yin, Lu, Gates & Xia, J. Am. Chem. Soc. 2001, 123, 8718
Highlighted as the Editors' Choice, Science, 2001, 293, 1560
Xia, Yin, Lu & McLellan, Advanced Functional Materials 2003, 13, 907

How Does a TASA Process Work?



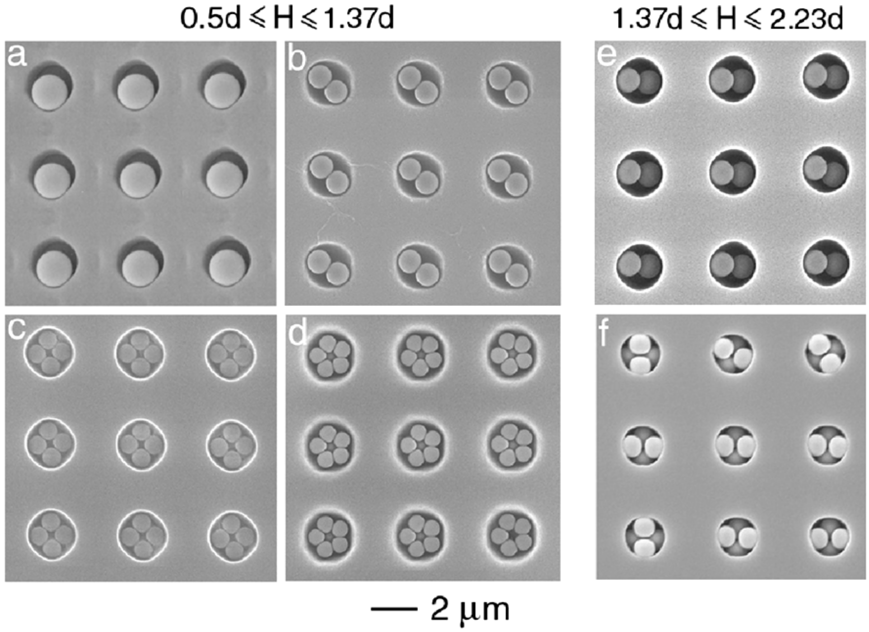
Attractive vs. Repulsive Interaction



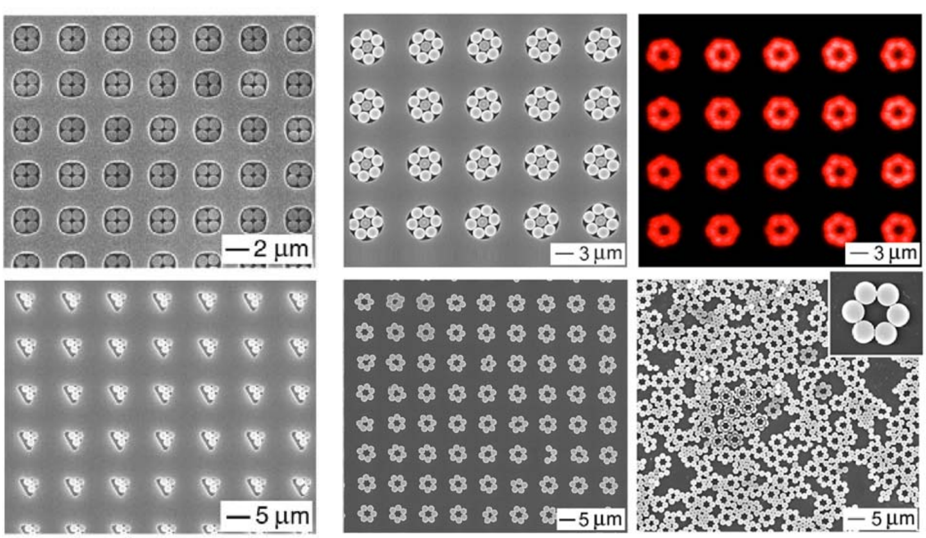
Control over the Self-Assembled Structures

D/d	Single-layered (0.5d ≤ H ≤ 1.37d)	Double-layered (1.37d ≤ H ≤ 2.23d)
1.00 - 2.00	monomer	dimer
2.00 - 2.15	dimer	tetrahedron
2.15 - 2.41	triangle	octahedron
2.41 - 2.70	square	bi-square-pyramid
2.70 - 3.00	pentagon	* Blue is the top layer
3.00 - 3.30	hexagon	* Red is the bottom layer

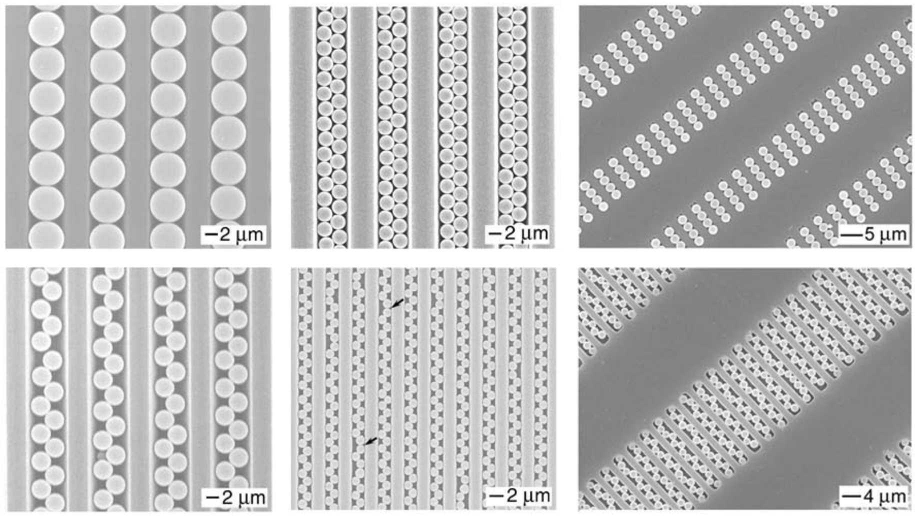
Examples of Polygonal and Polyhedral Clusters



Templates with Different Cross-Sections

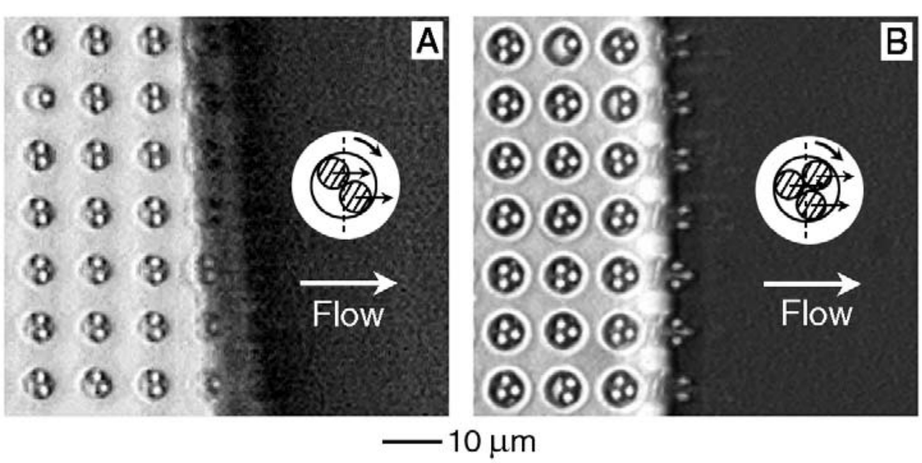


Linear and Zigzag Chains of Polystyrene Beads

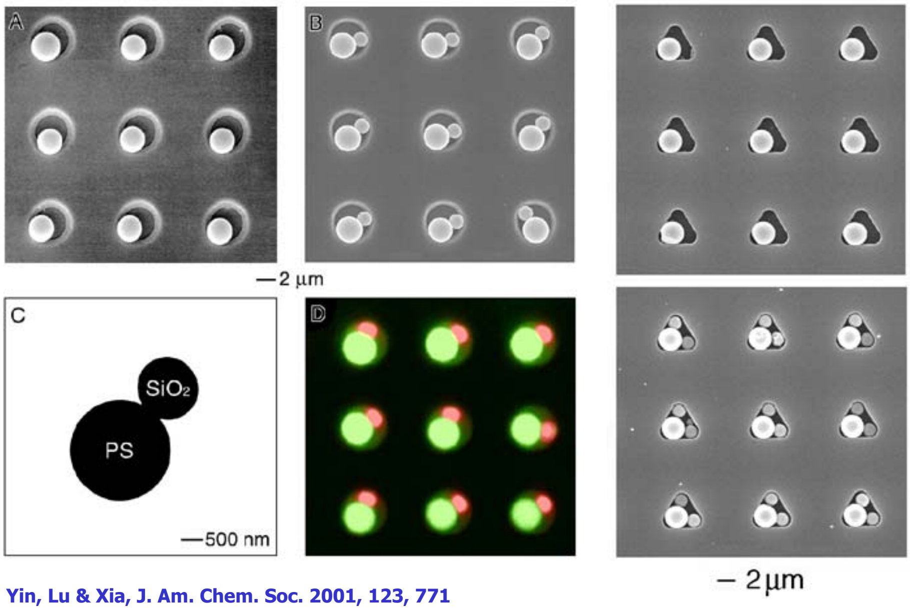


Yin, Lu & Xia, Journal of Materials Chemistry 2001, 13, 1146

Control over the Spatial Orientation of Clusters

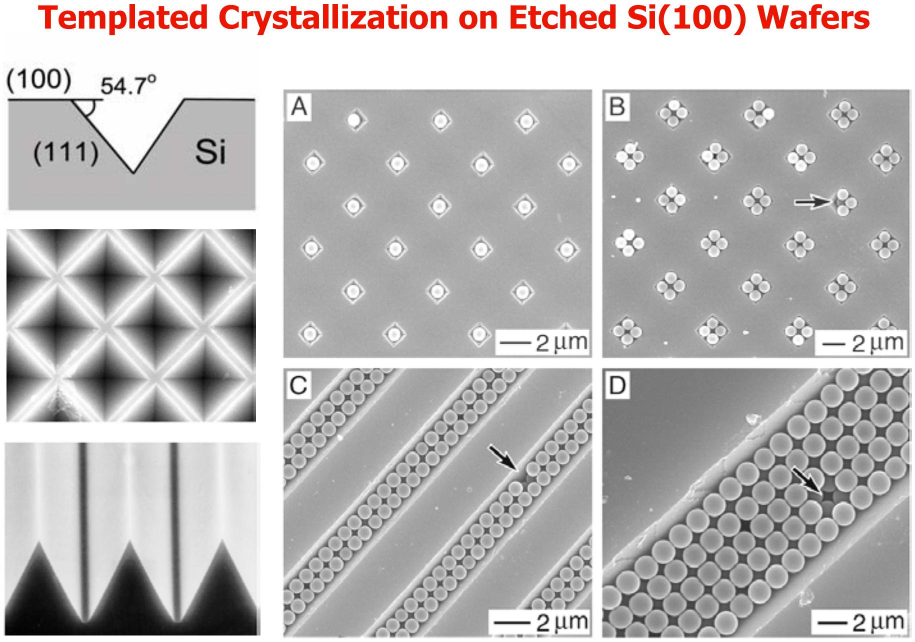


Hybrid Clusters Consisting of Different Colloids

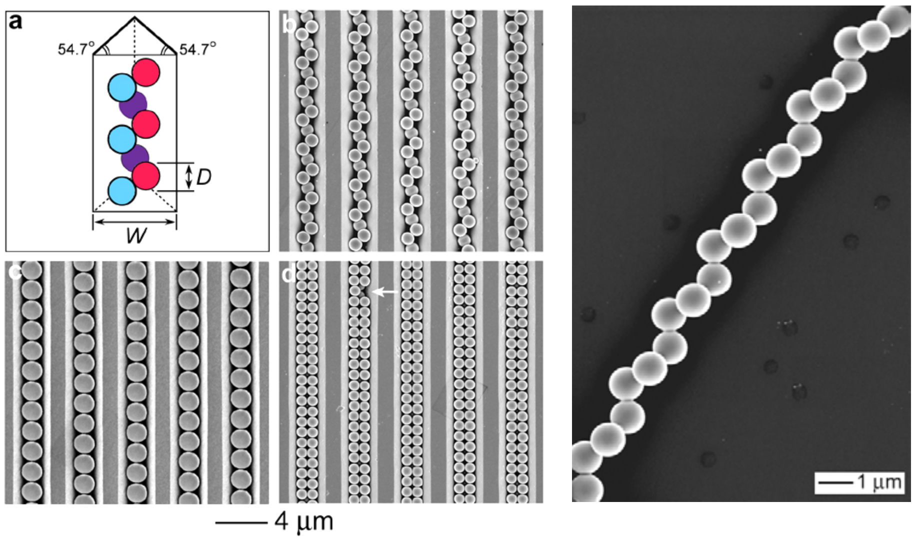


Yin, Lu & Xia, J. Am. Chem. Soc. 2001, 123, 771

Templated Crystallization on Etched Si(100) Wafers

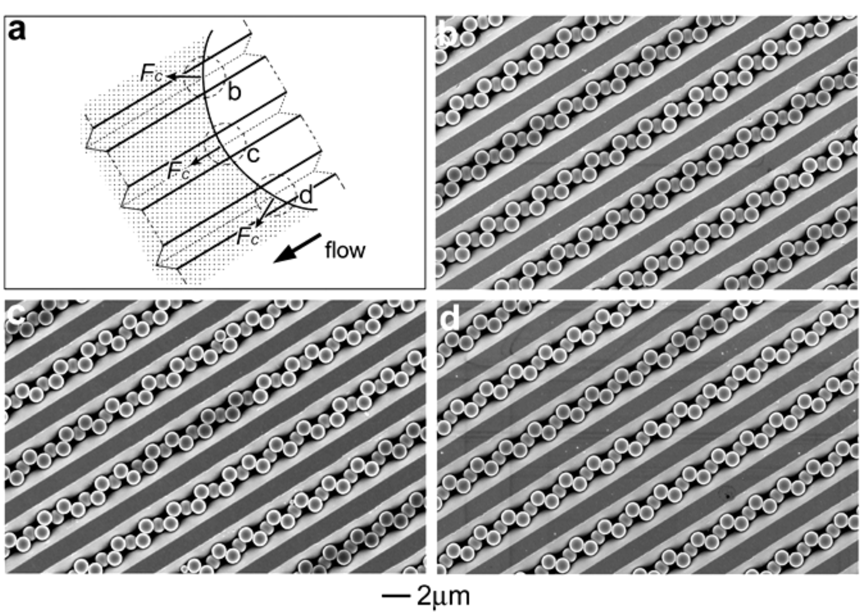


Assembly of Spherical Colloids into Spiral Chains

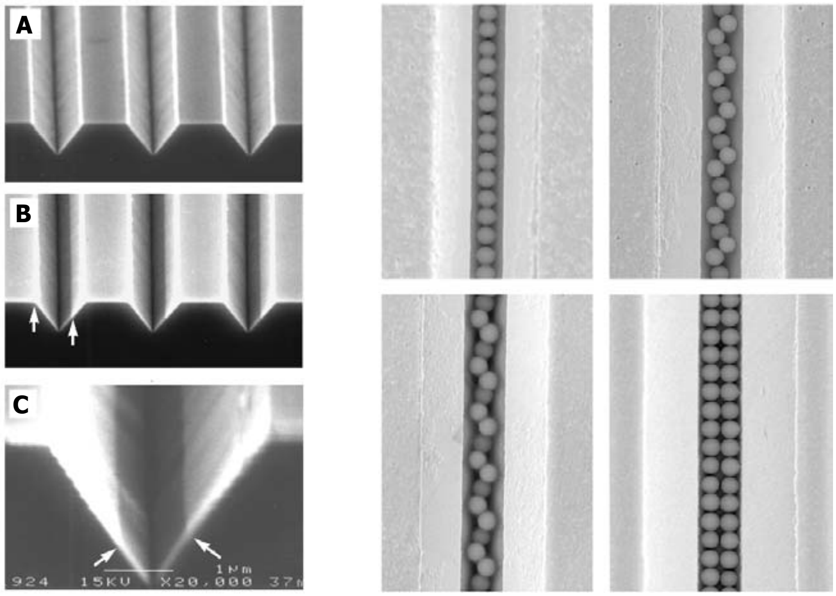


Yin & Xia, J. Am. Chem. Soc. 2003, 125, 2048

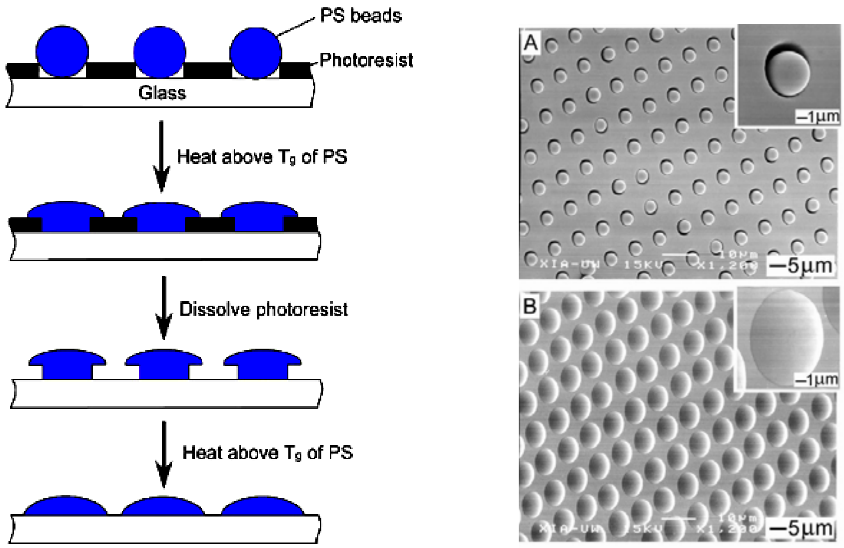
Control over the Exact Optical Handedness



Self-Assembly of 360-nm Silica Beads

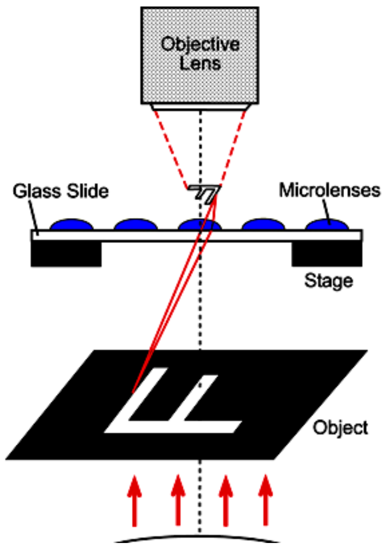


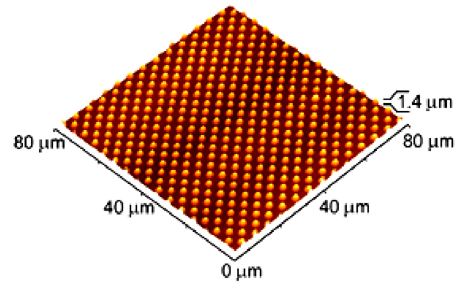
Fabrication of Arrayed Polymer Microlenses

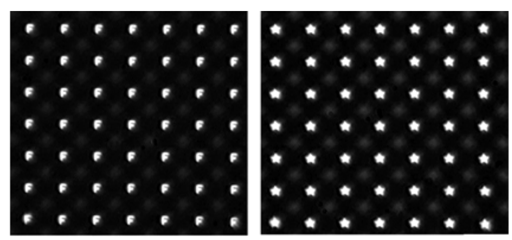


Lu, Yin & Xia, Advanced Materials 2001, 13, 34

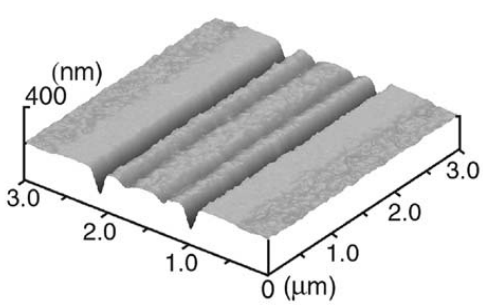
Imaging through Arrayed Polymer Microlenses







Extension to Smaller Scales?



An Array of ~120 nm Channels by Near-Field Photolithography