SAND2012-9860P

# Materials Xenoscience: Exploring Emergent Materials at Non-Traditional Interfaces Between Materials Science and Biology


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**Sandia National Laboratories**


**13 November, 2012**

**Department Seminar**
**Chemical and Nuclear Engineering**
**University of New Mexico**

# Seminar Tour Guide

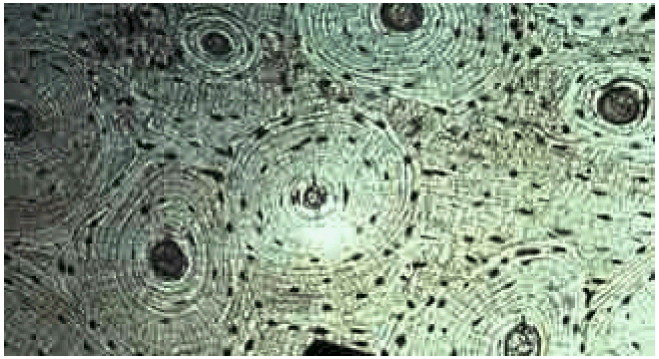
I. Peptides and Biomolecules as Molecular Modifiers

II. Mimicking Biomineralization

III. Utilizing Biomaterials for Nanomaterials Assembly and Organization

# Why Use Peptides to Direct Materials Synthesis?

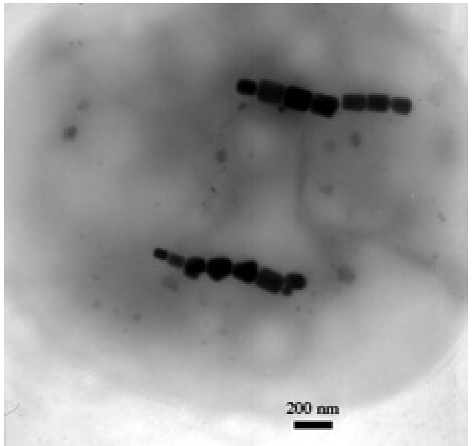
Compact bone



http://www.engin.umich.edu/class/bme456/bonestructure/bonestructure.htm

Nature uses amino acids as the building blocks of complex proteins that regulate and influence inorganic crystal growth and function.

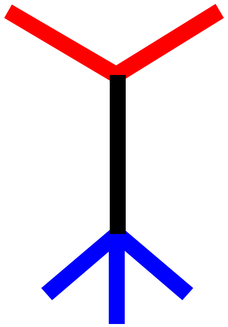
Magnetotactic bacteria




http://www.biophysics.uwa.edu.au/STAWA/TEM_images.html

How can we use amino acid building blocks to direct the synthesis and function of engineered materials?

# A “bio-inspired” peptide design

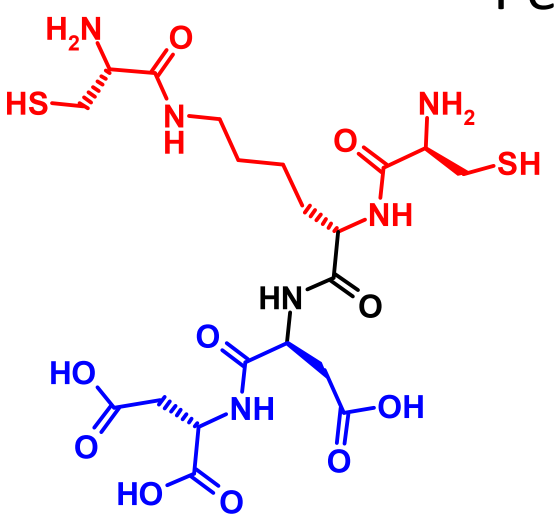


**Branches: Reactive Groups**

**Trunk: Inert Spacer**

**Roots: Functional Groups**

Peptide: DDKCc



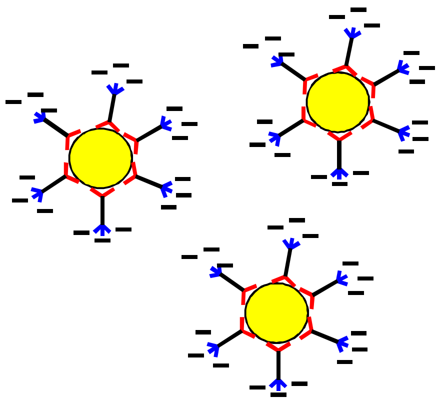

Cysteine Branches

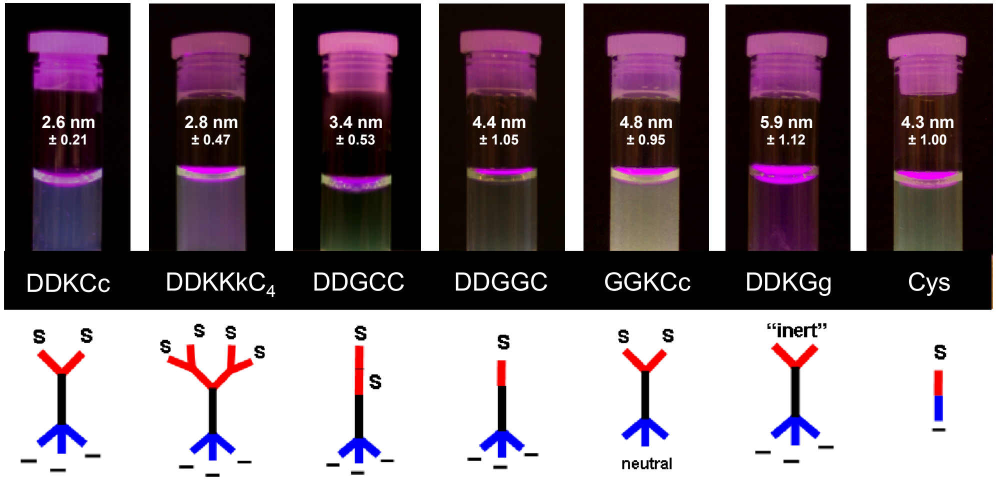
Short, Inert Trunk

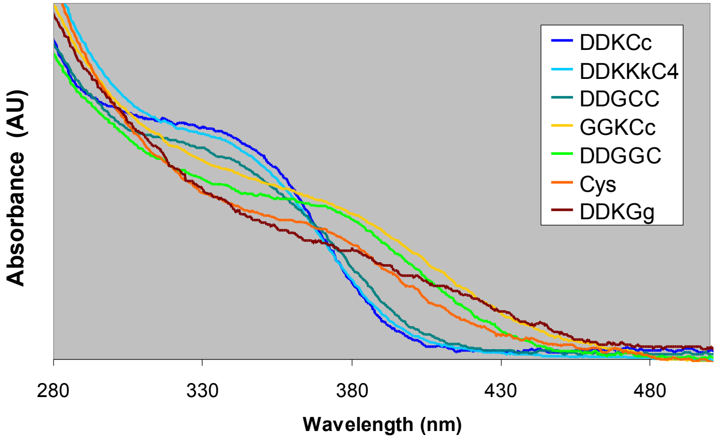
Aspartic Acid Roots

# Using Peptides to Control Cadmium Sulfide Nanocrystal Capping

Branched, functional peptides can be tuned to control optoelectronic properties by controlling nanoparticle size.





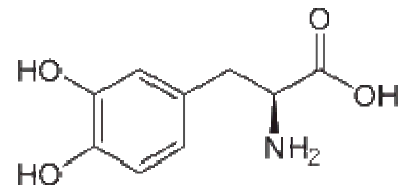



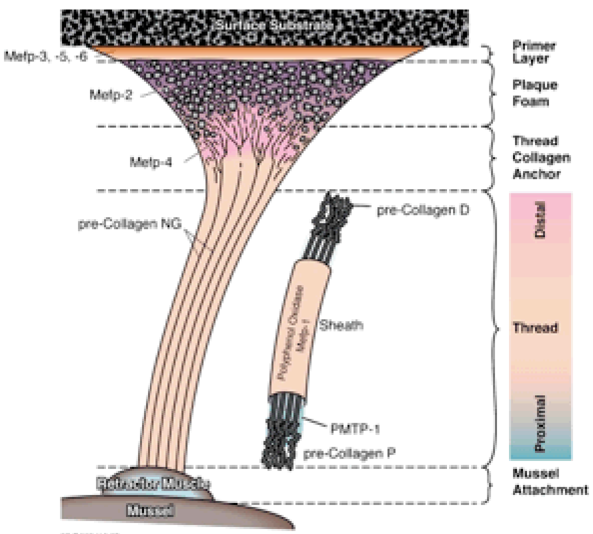

Spoerke, et al. Adv. Funct. Mater. (2007) **17** (13). 2031-2037.

# Peptide Design for Surface Adhesion/Modification

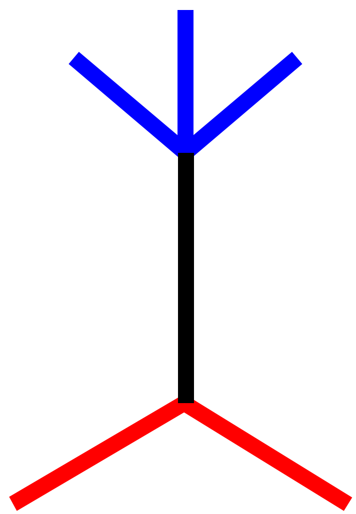
mistra-research.se

Aquatic organism like mussels bind to surfaces using proteins rich in 3,4 dihydroxyphenylalanine (DOPA)




Silverman, et al. Mar Biotechnol. 2007; 9(6): 661–681.



**Adhesive DOPA Roots**

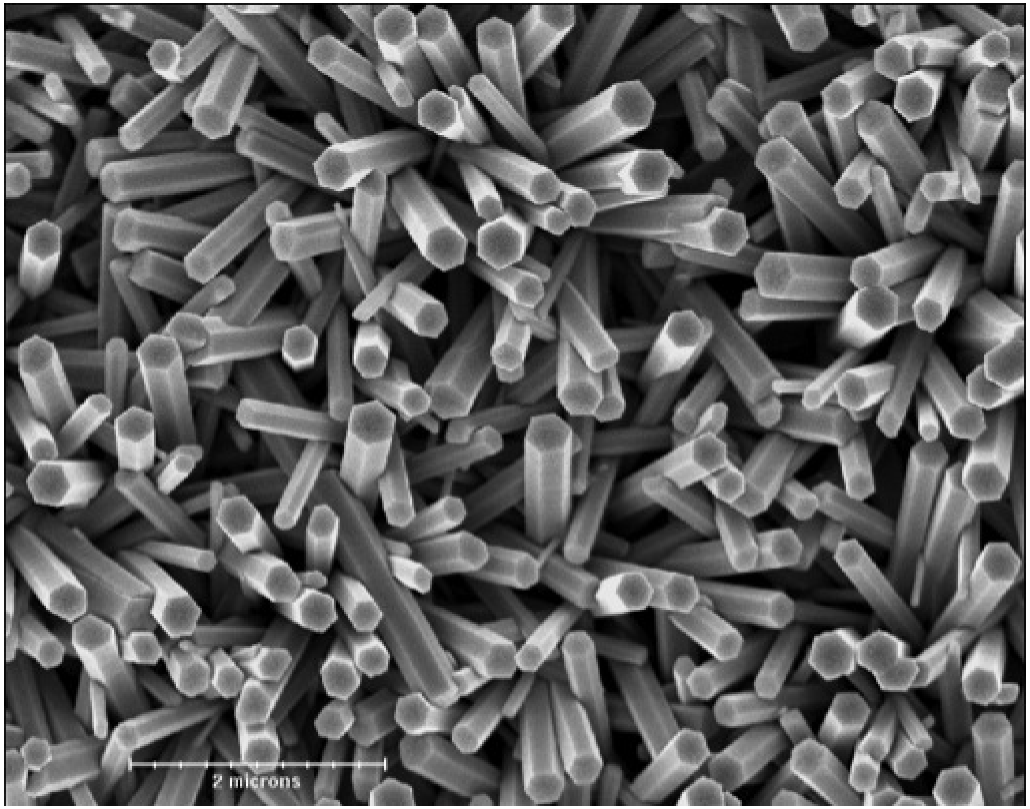
**Inert Trunk**

**Functionally Rich Branches**

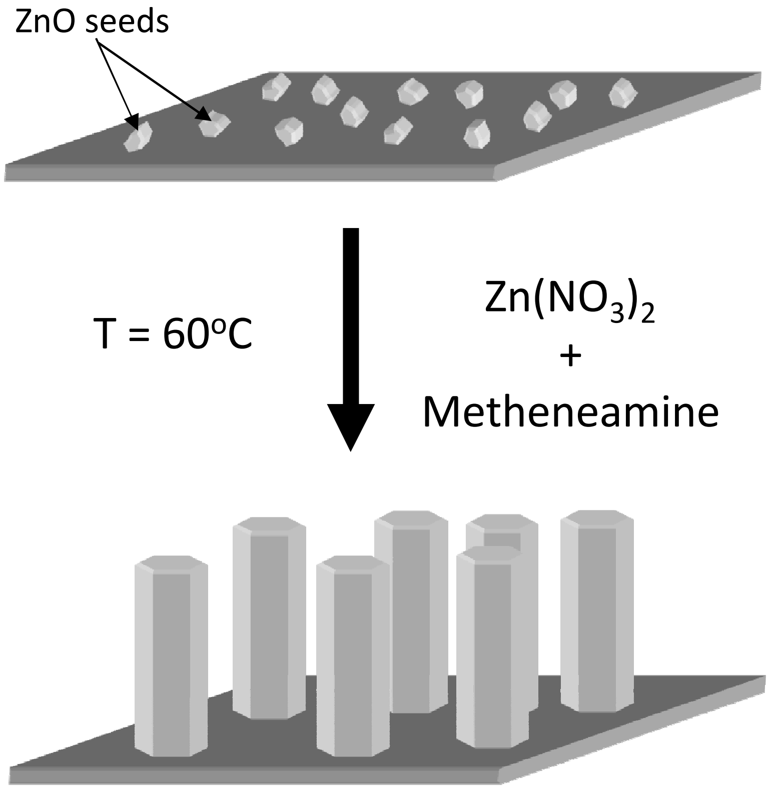
# Peptide Selectivity to ZnO

## ZnO rod growth

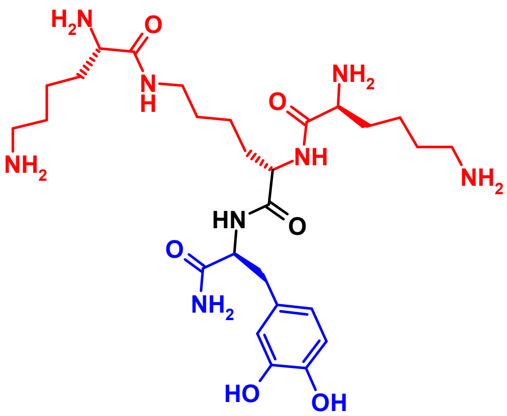
ZnO rods grown on glass



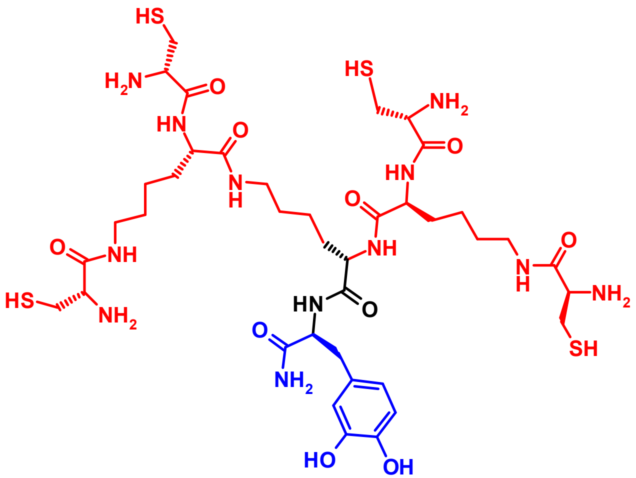

Hydrothermal ZnO synthesis



# Functionalization of ZnO with DOPA-peptides



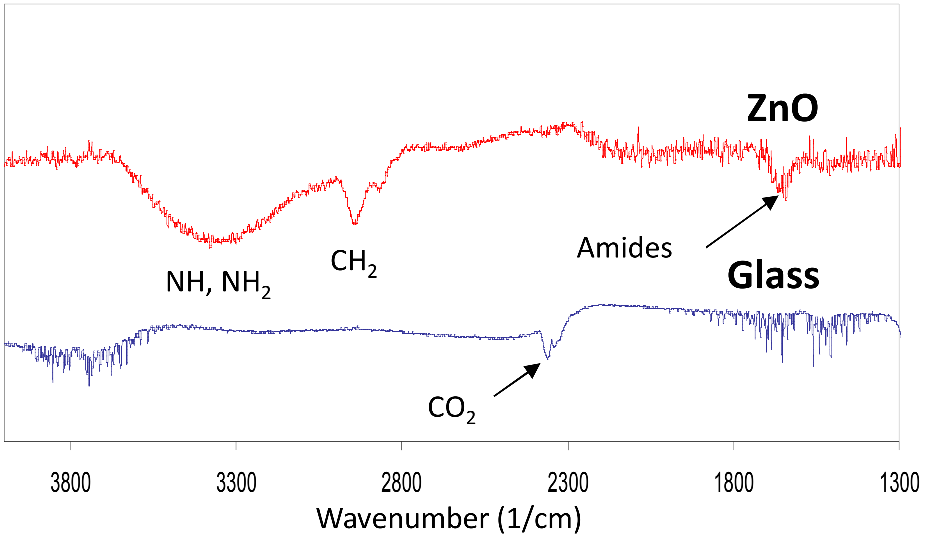

DopaKKk




DopaK2C4

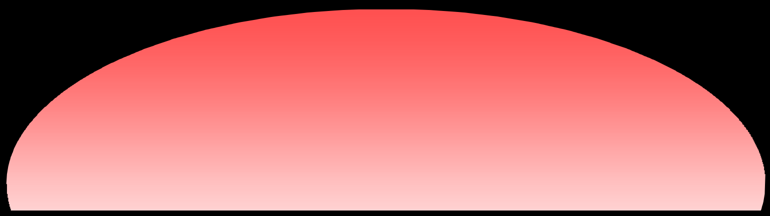
DOPA-based peptides, enriched with amines and thiols can be selectively bound to ZnO

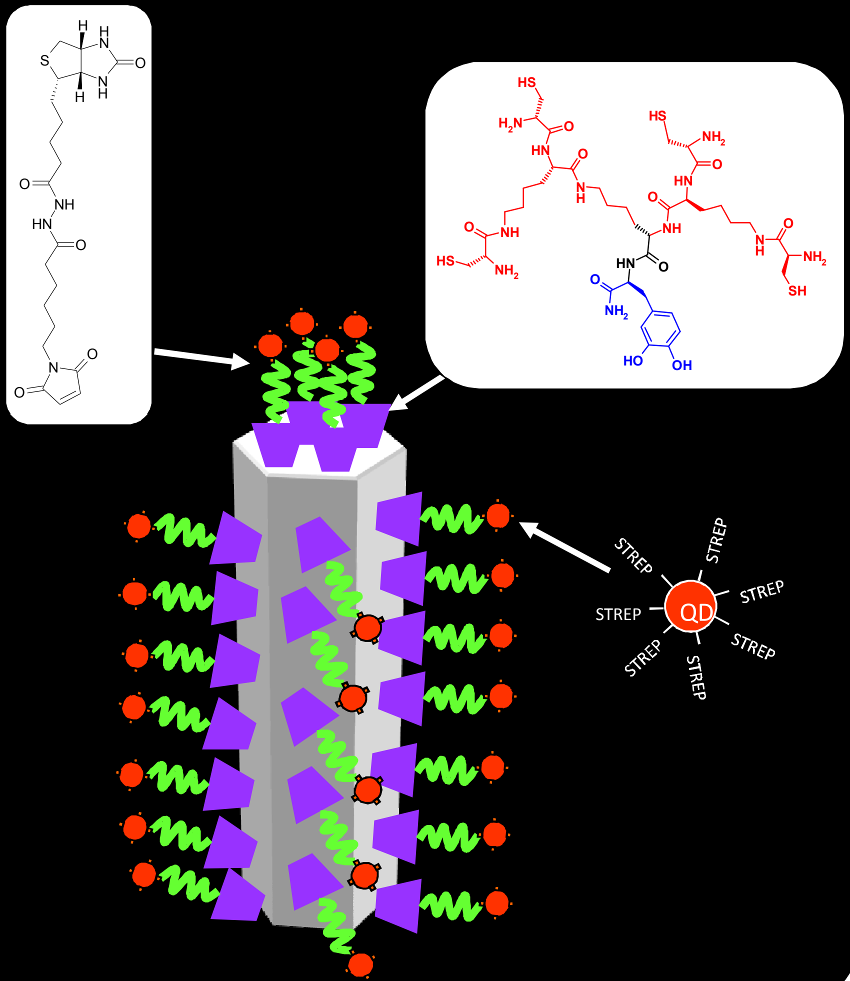
**FTIR**



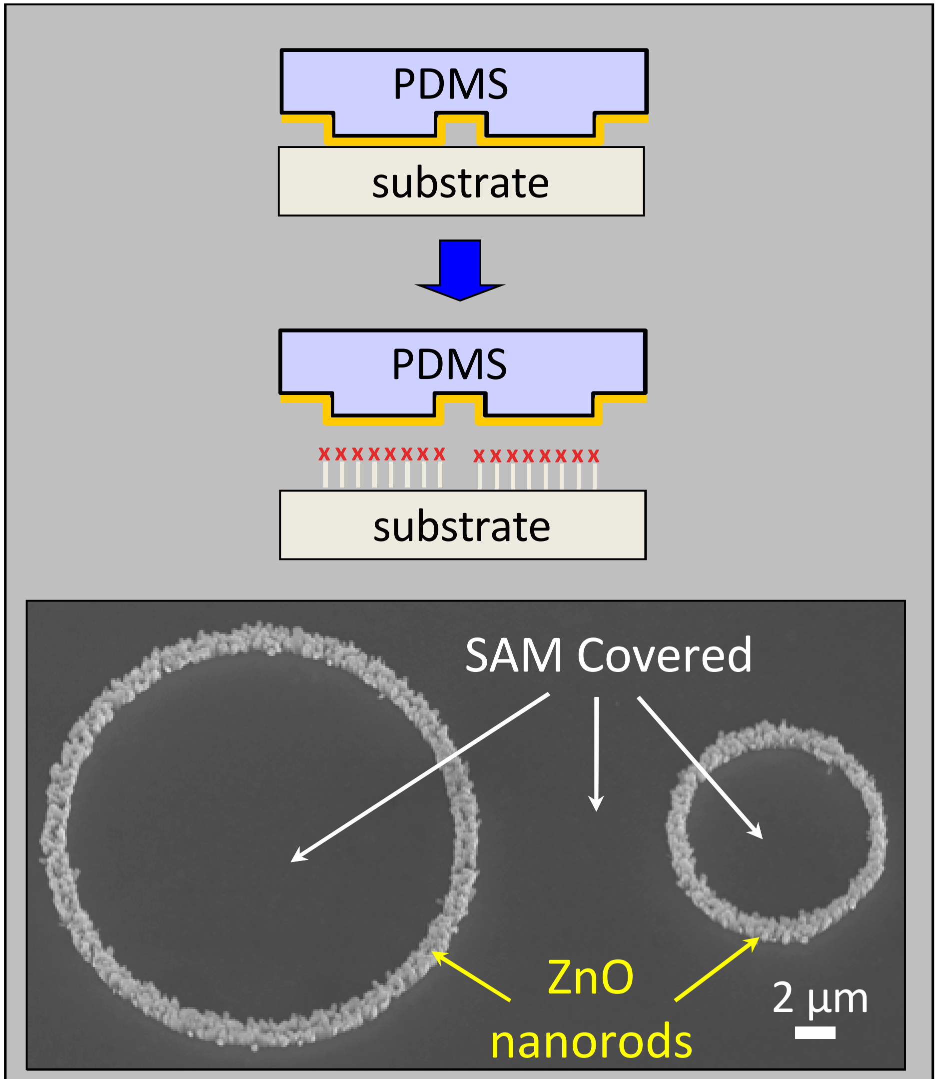
# Scheme for Controlling Attachment of Nanoparticles to ZnO

Sequential incubations of ZnO-patterned substrates with DOPA peptides, chemical linkers, and functional nanocrystals enable particle templating on ZnO.

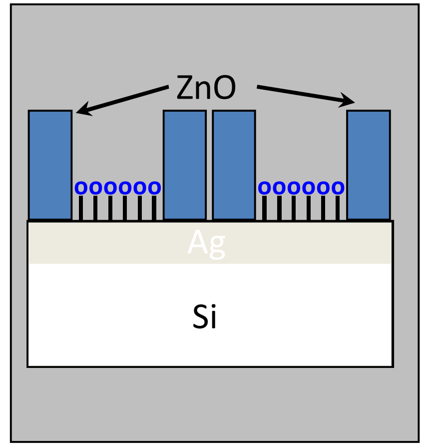


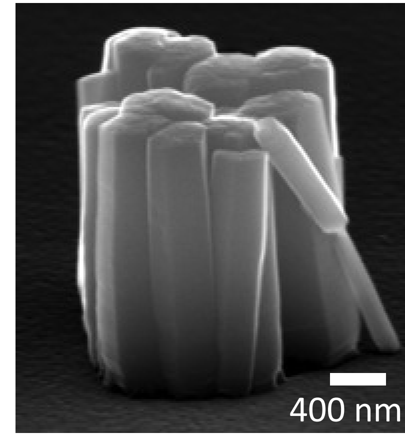


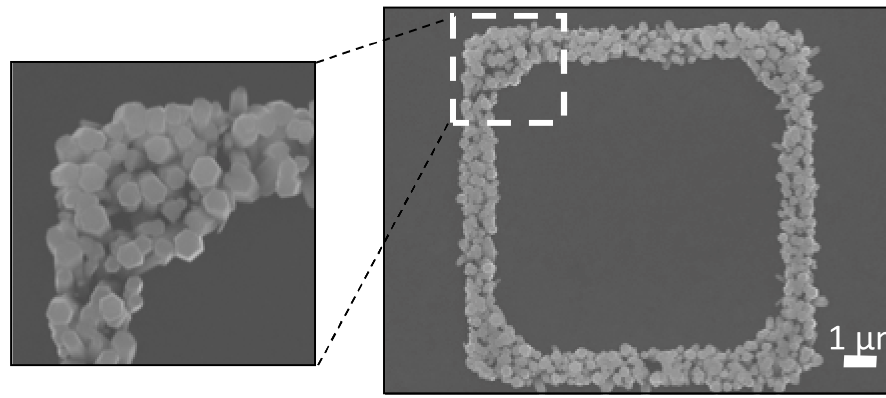
# Microcontact Printing to Pattern ZnO Nanorod Growth




Hsu, et al. *Nano Lett*. 5, 83-86 (2005)

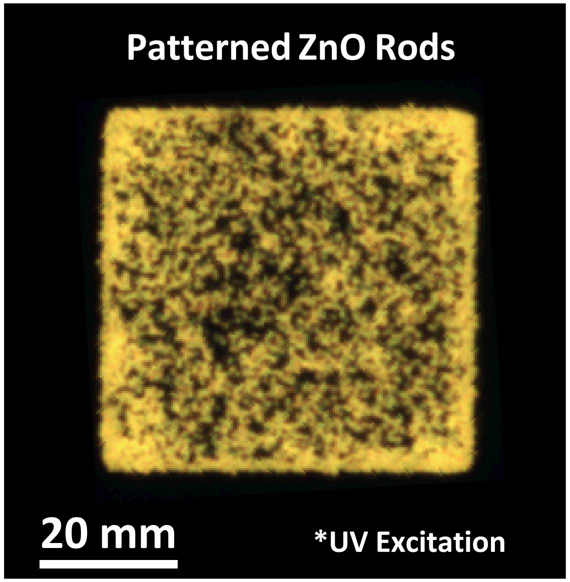


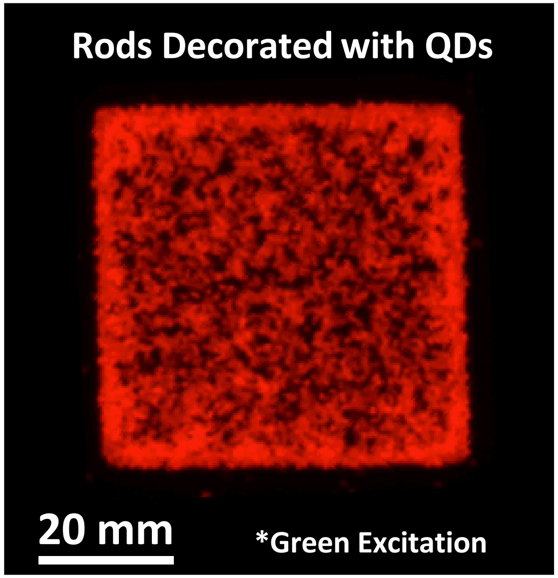



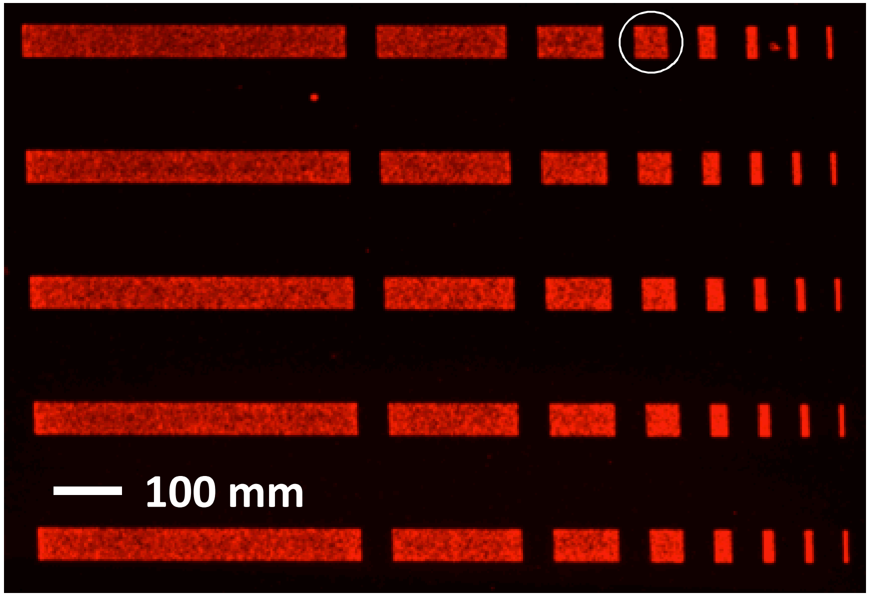

Microcontact printing allows for selective, aqueous growth of patterned, vertical ZnO rods

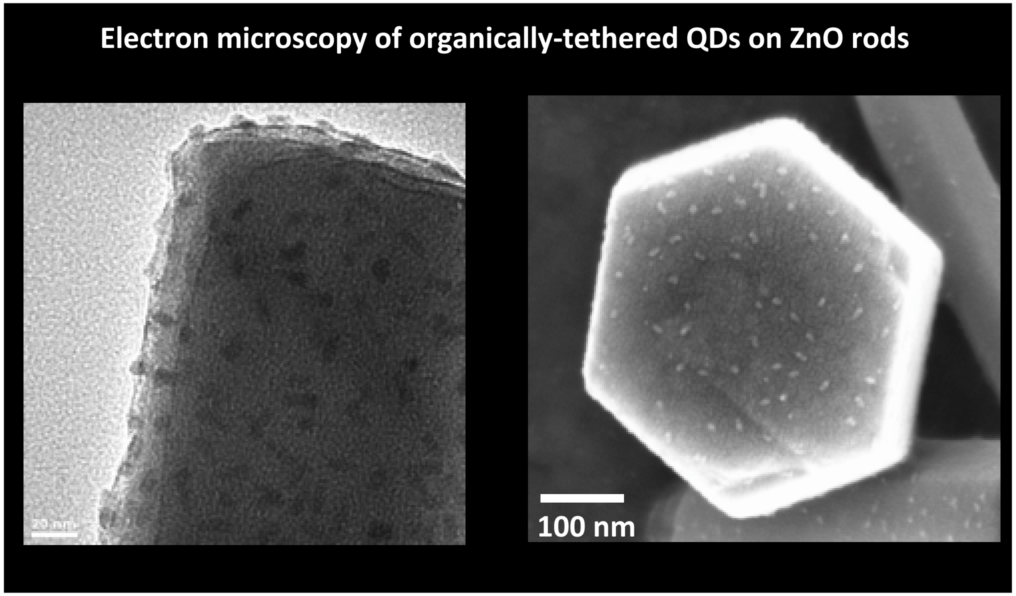
# Decorating Patterned ZnO Rods with Quantum Dots



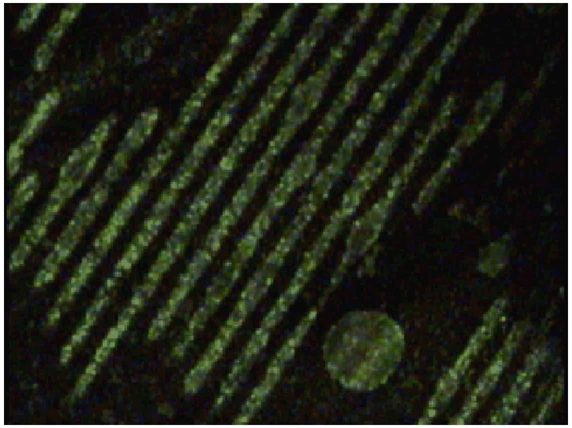

**Functionalize the ZnO and attach QDs**

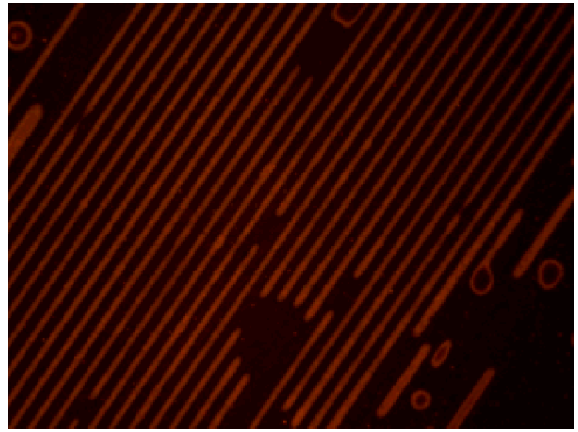


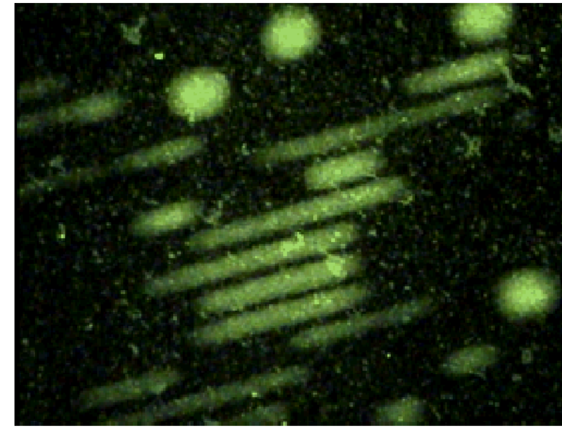



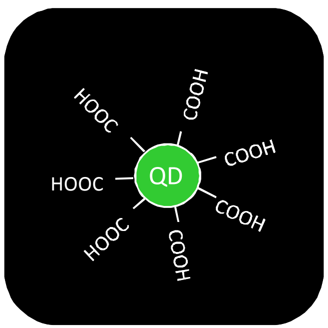



# Chemical Versatility of the Approach







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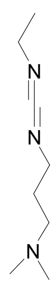
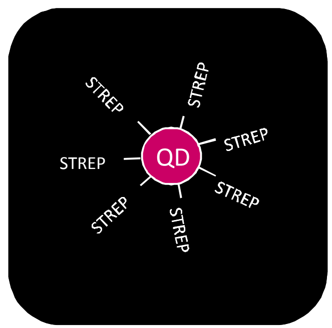


EDCI

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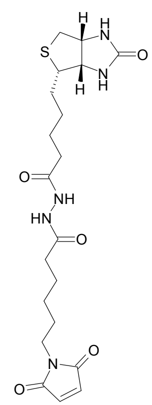
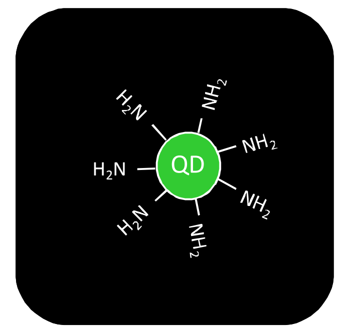


Biotin-
Maleimide

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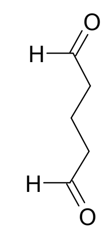
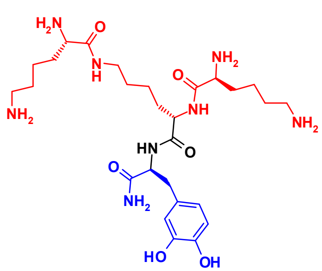
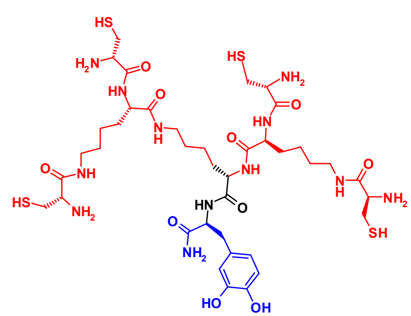
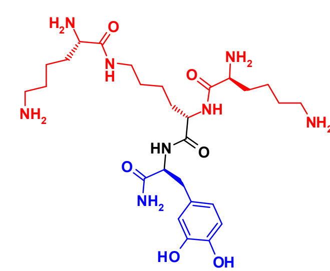


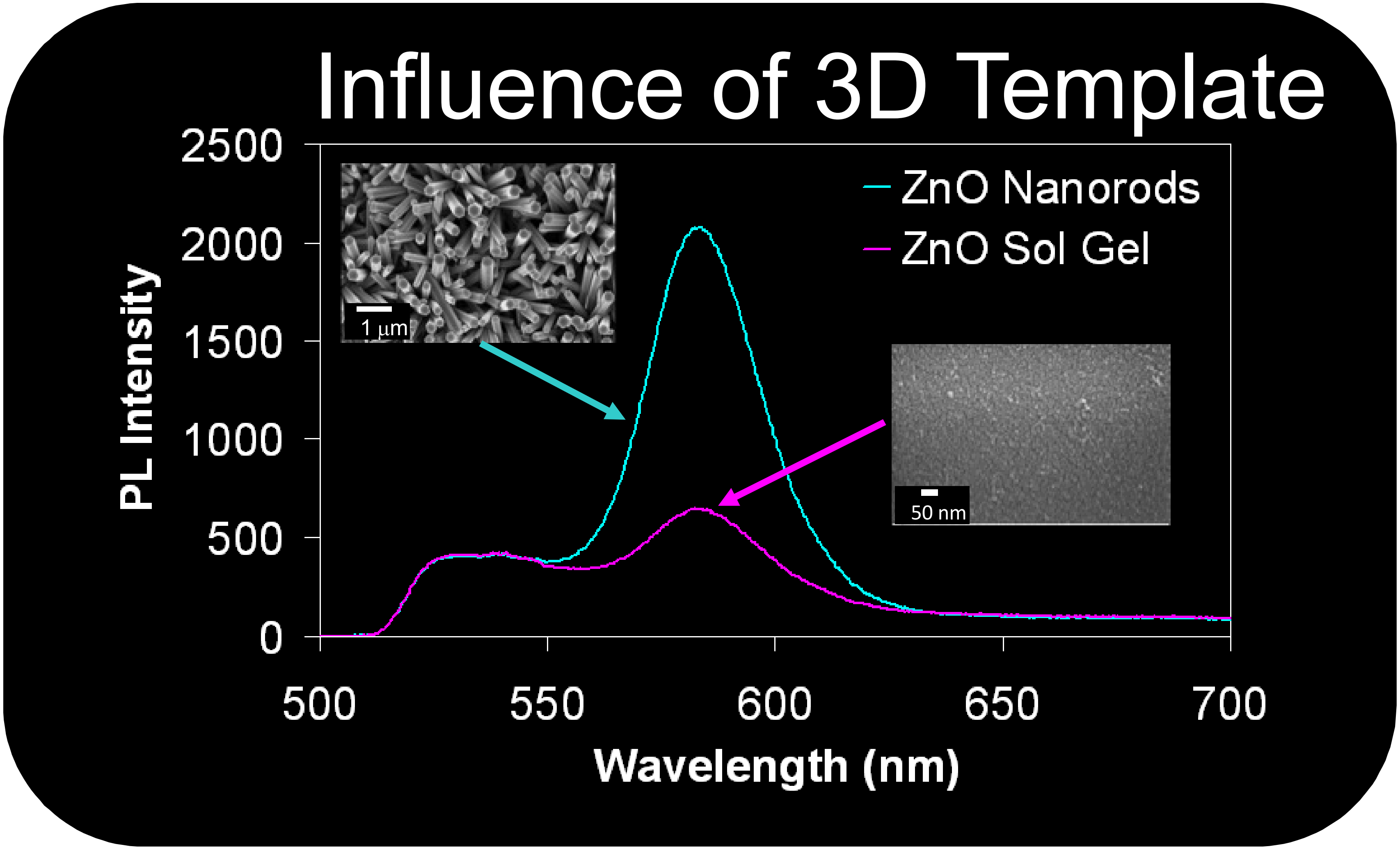
Glutaraldehyde







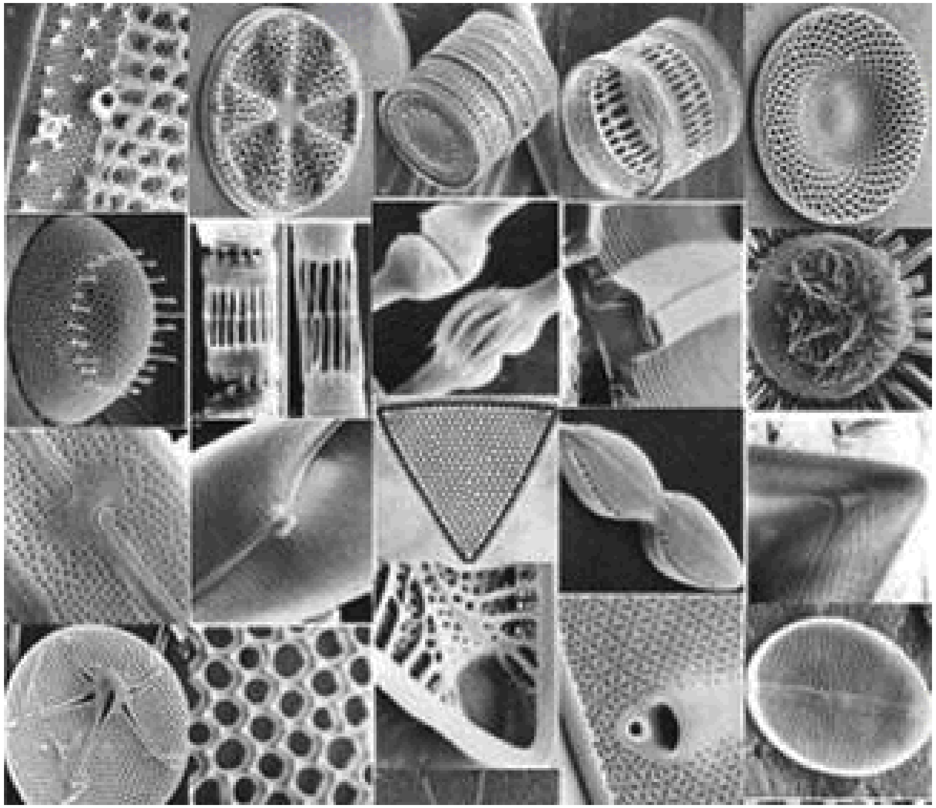
# "Very nice.  Who cares?"




The ability to tailor chemistry for controlled binding of target nanoparticles on ZnO nanorod arrays has implications for enhanced catalysis and sensing.

# Biomineral Inspiration

**Diatoms made of silica**

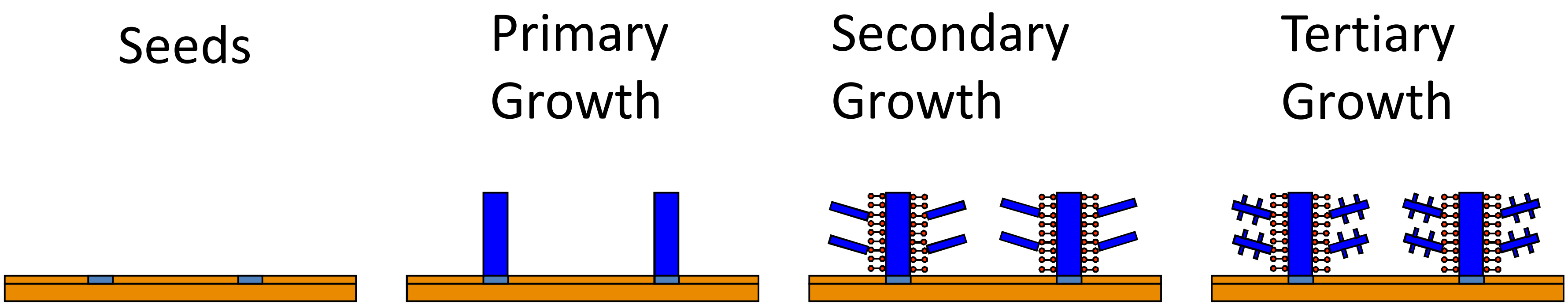


*Can we combine our DOPA peptides with ZnO and silica chemistry to make "synthetic diatoms"?*

Round, Crawford, Mann, "The Diatoms: Biology and Morphology of the Genera", 1990

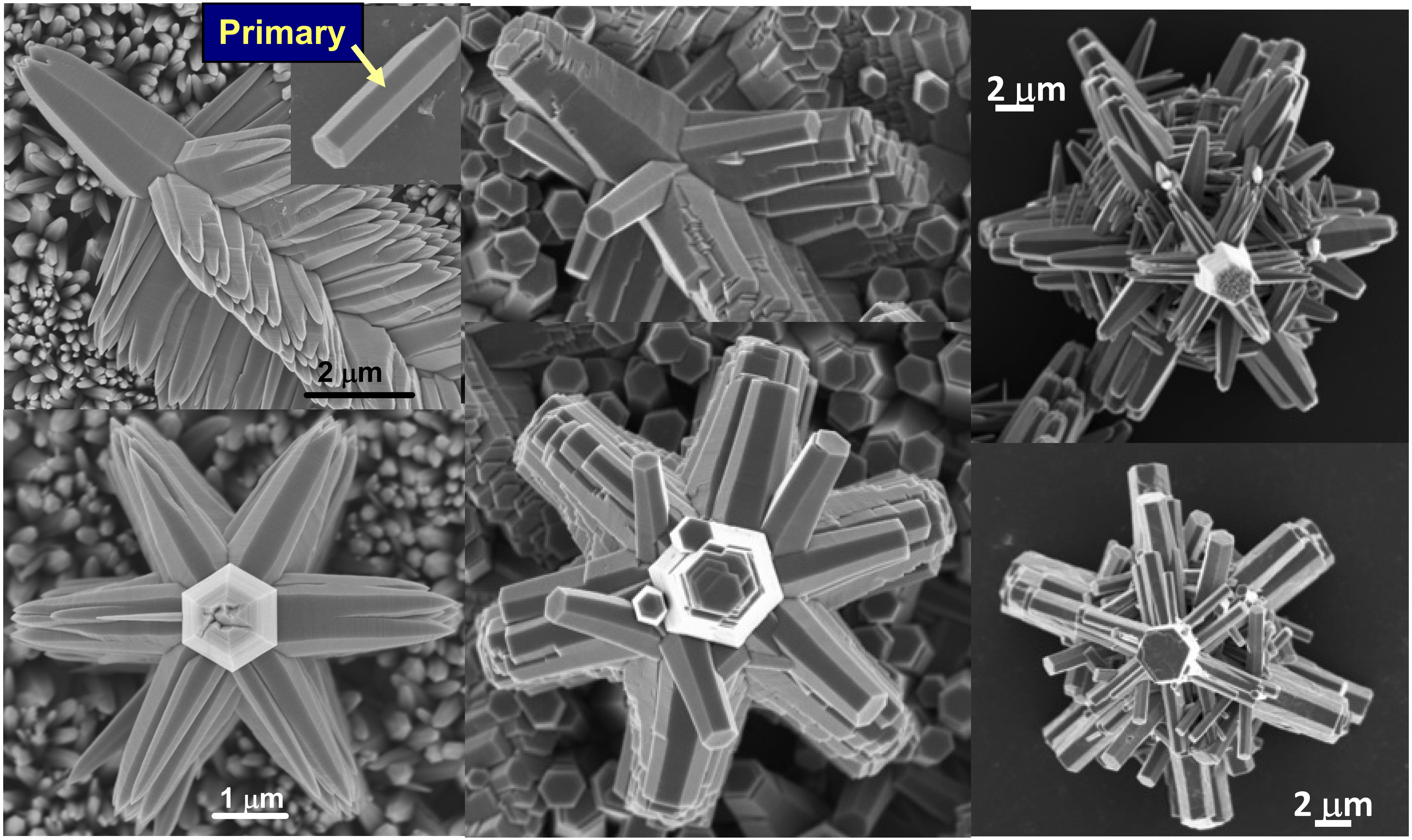
# Complex ZnO Templates

Using sequential nucleation and growth chemistry, coupled with aminoalkane growth modifiers, we can create complex ZnO architectures.



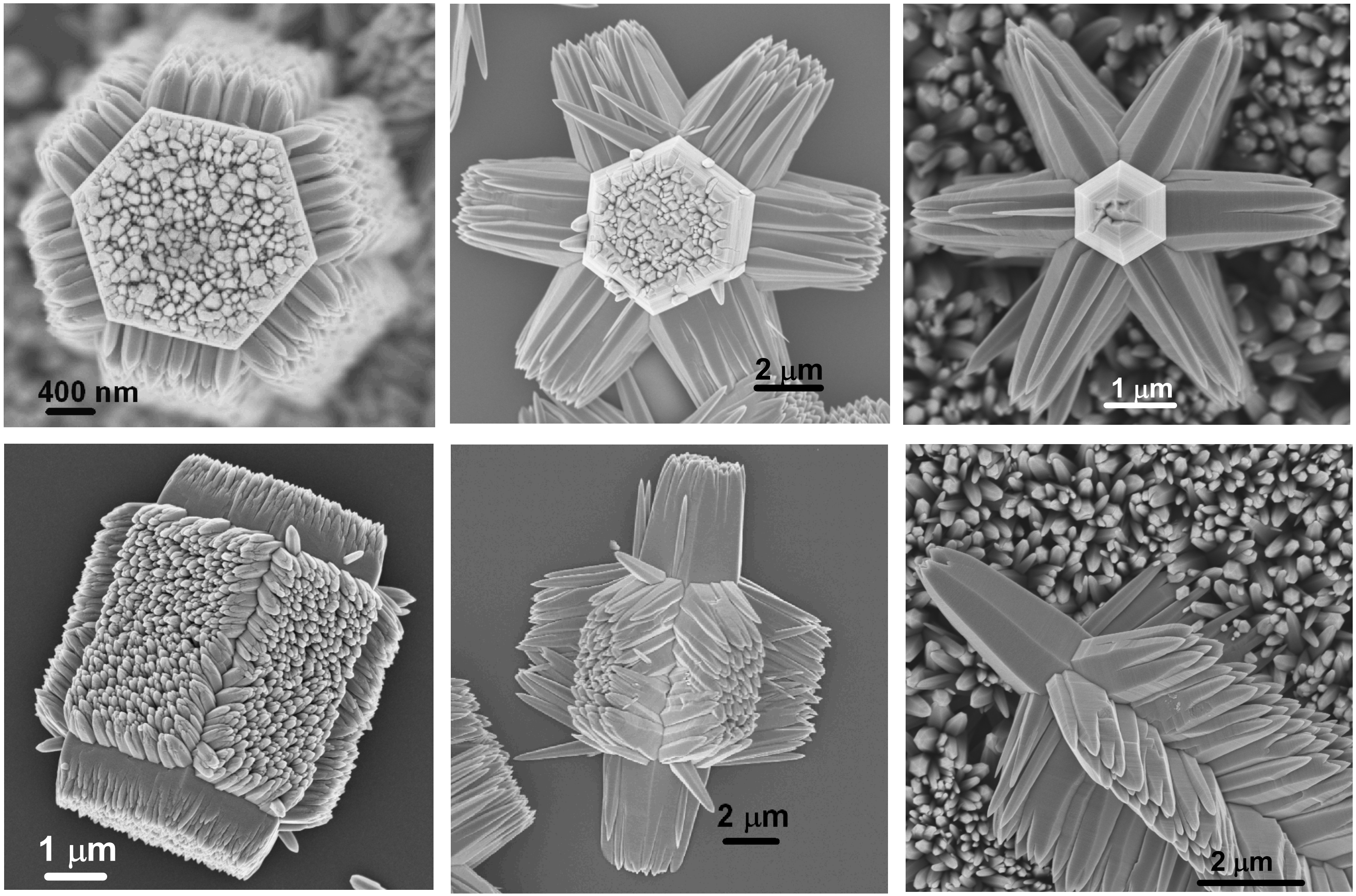
# Higher-Order Structures: Sequential Nucleation and Growth

**Secondary Structure** **Healed Secondary** **Tertiary Structure**




**Diaminoalkanes (e.g. ethylene diamine, diaminopropane, diaminobutane)**

# Organic Modifiers:  Effect of Diamine Concentration



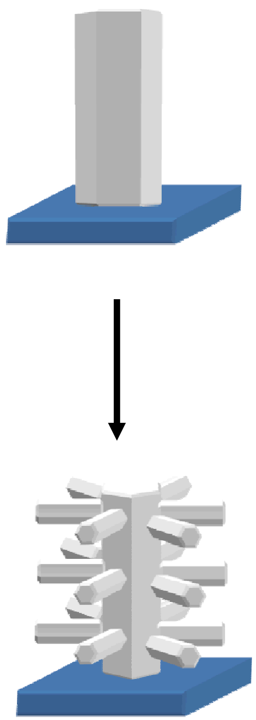

**Increasing Diamine Concentration**

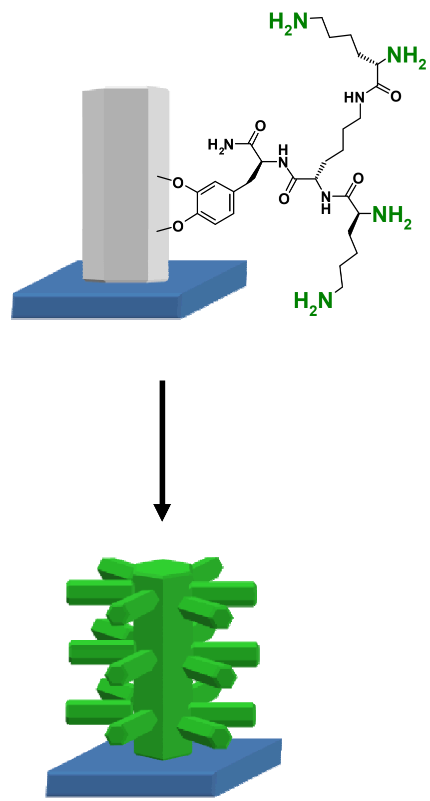
# Engineering Templated Silica Growth and Assembly

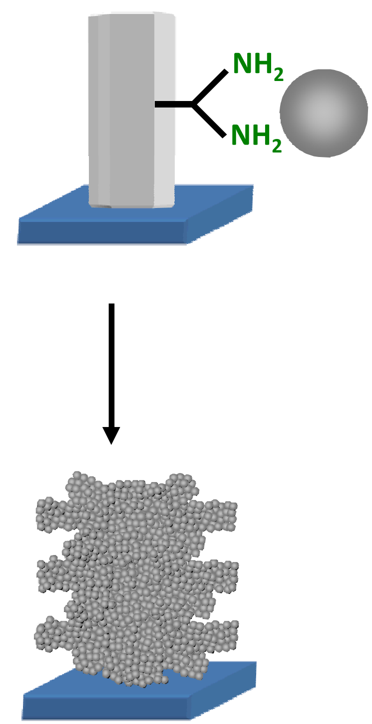
Multi-stage nucleation and growth used to grow ZnO templates

Engineered peptides used to protect and functionalize ZnO with amines

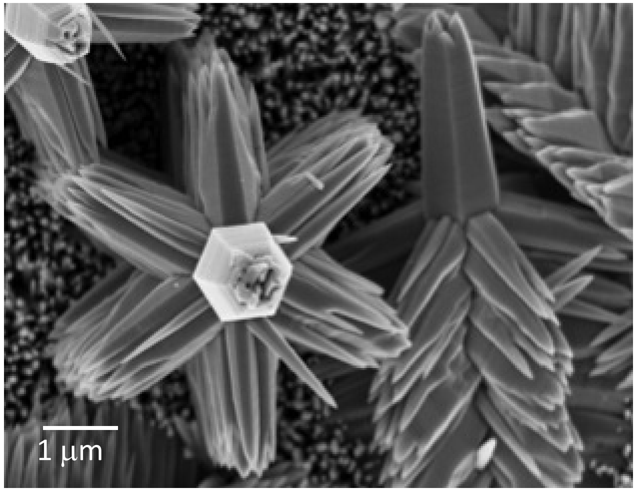
Amine-catalyzed silane chemistry produces templated silica architectures.



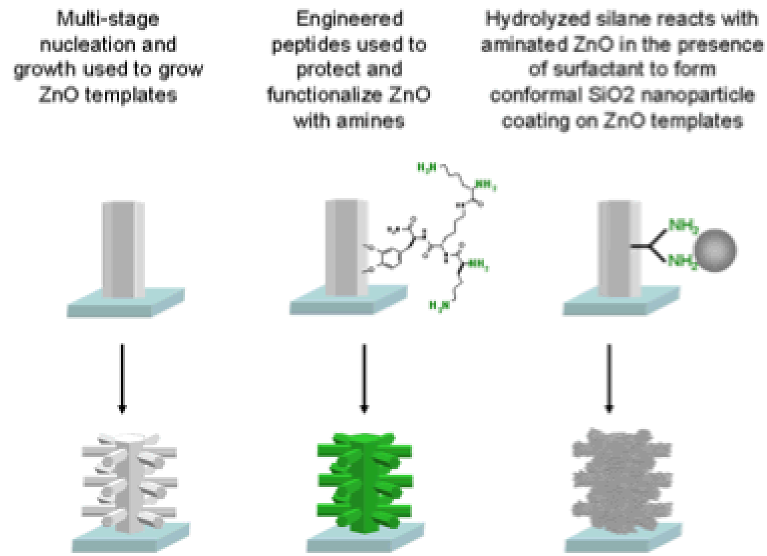


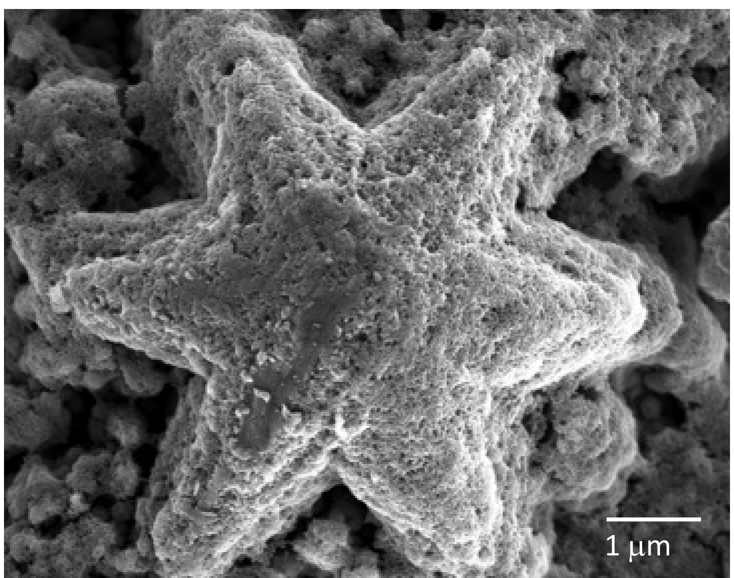



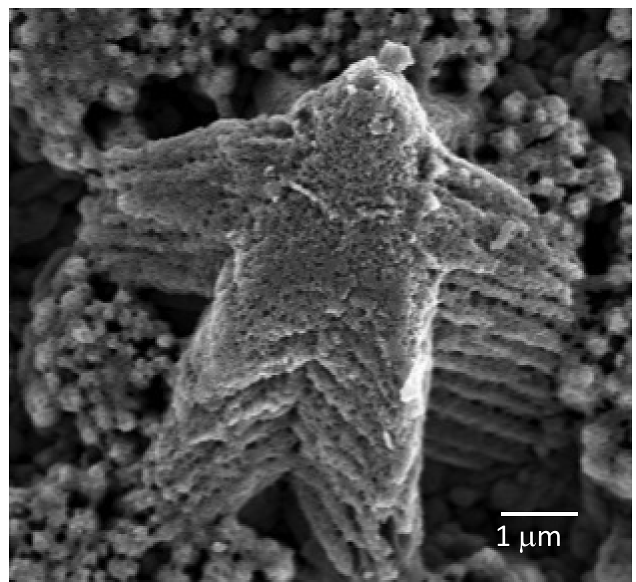
# ZnO-Templated $SiO_2$ Composite Architectures

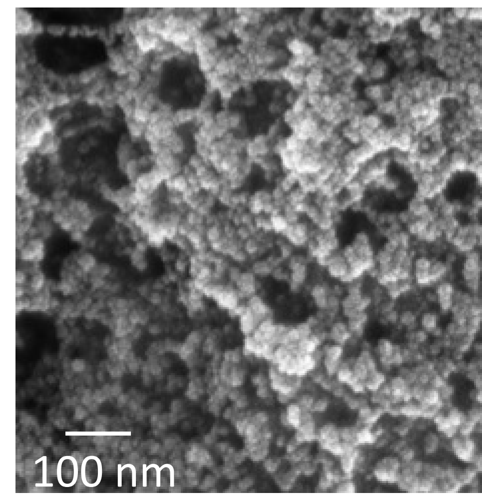



ZnO template architectures, prior to silica growth




$SiO_2$ coating is composed of nanoparticles less than 10 nm in diameter

Silica nanoparticles grown conformally on ZnO templates with complex structure

# CdS in Photovoltaics

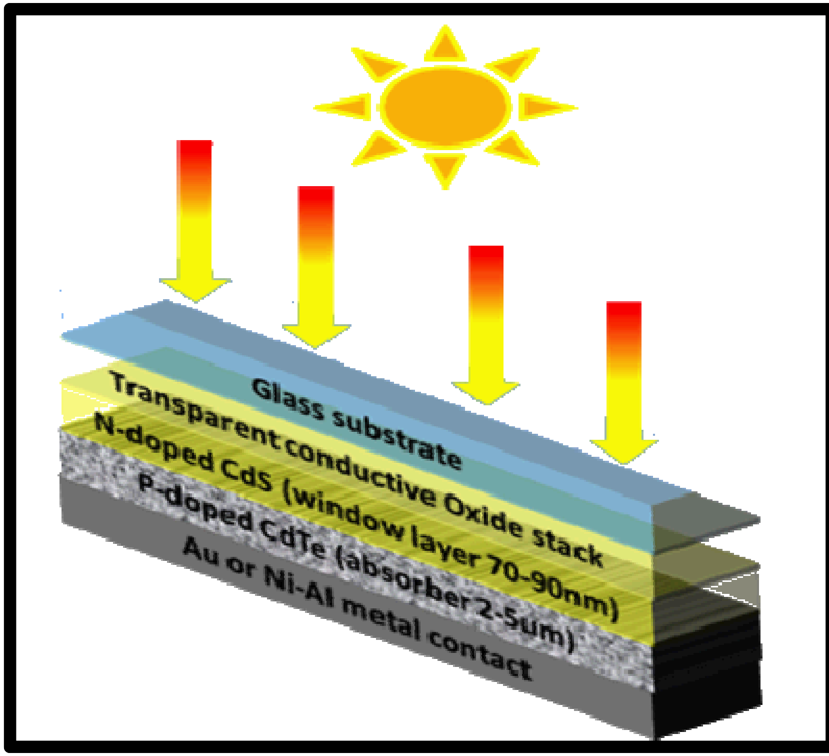
Cadmium sulfide is a key component in thin film photovoltaics (PV)

- *CdTe*
- *InP*
- *CIGS*
- *Hybrid OPV*

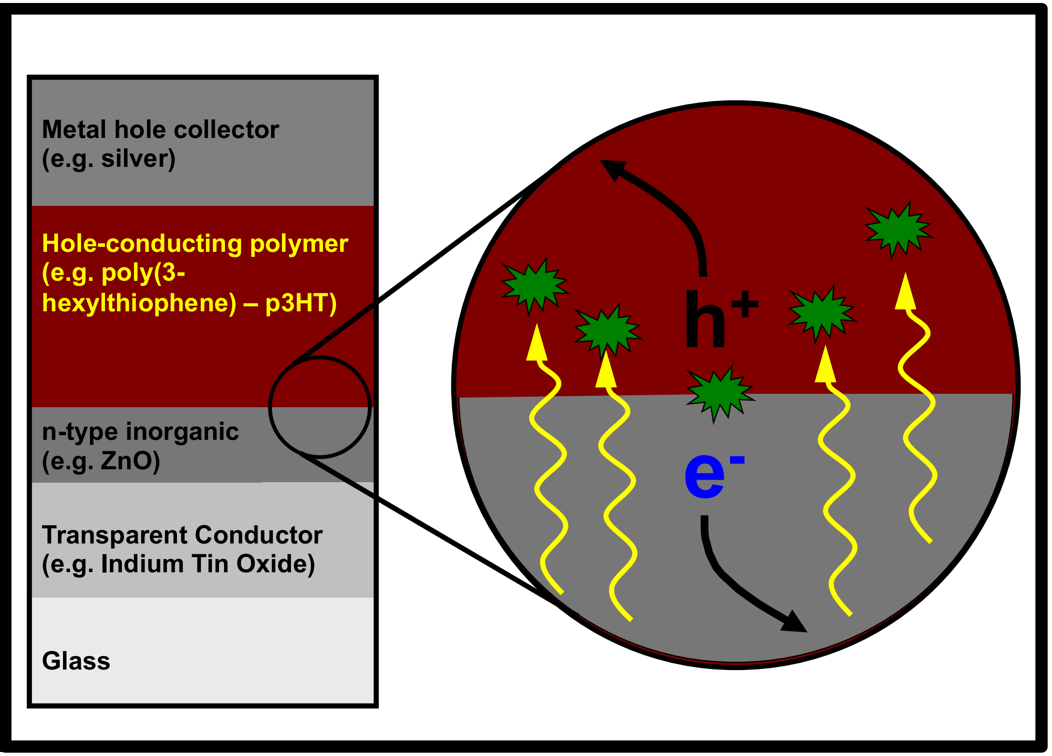
**Key CdS Characteristics**

- ✧ Proper energy band alignment
- ✧ Dense
- ✧ Thin
- ✧ Inexpensive, controllable growth

## CdTe PV

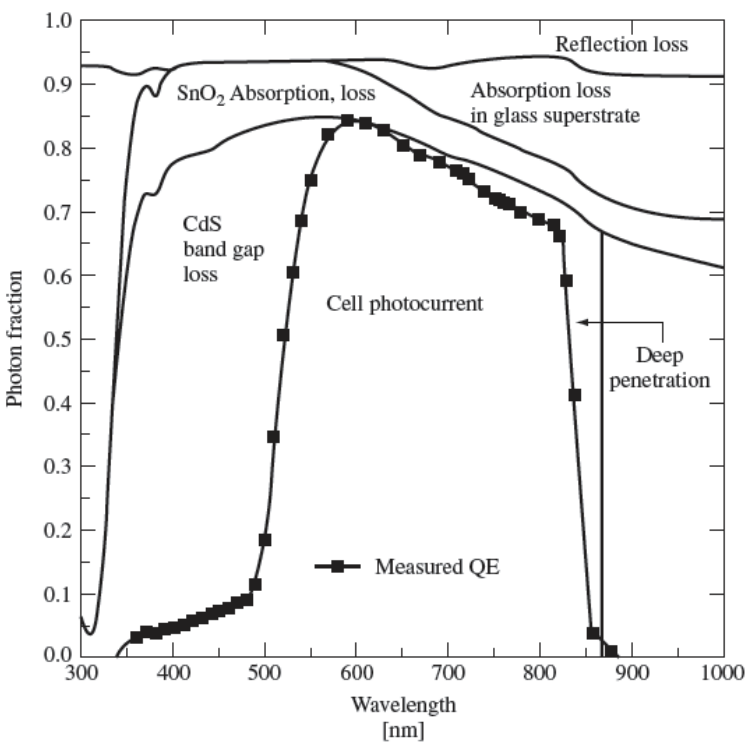



## Hybrid OPV



# Parasitic Absorbance of CdS in PV devices

CdS has a band gap ~2.4 eV, which leads to parasitic absorbance below ~515 nm.




To address this problem CdS must be thin, but conformal.

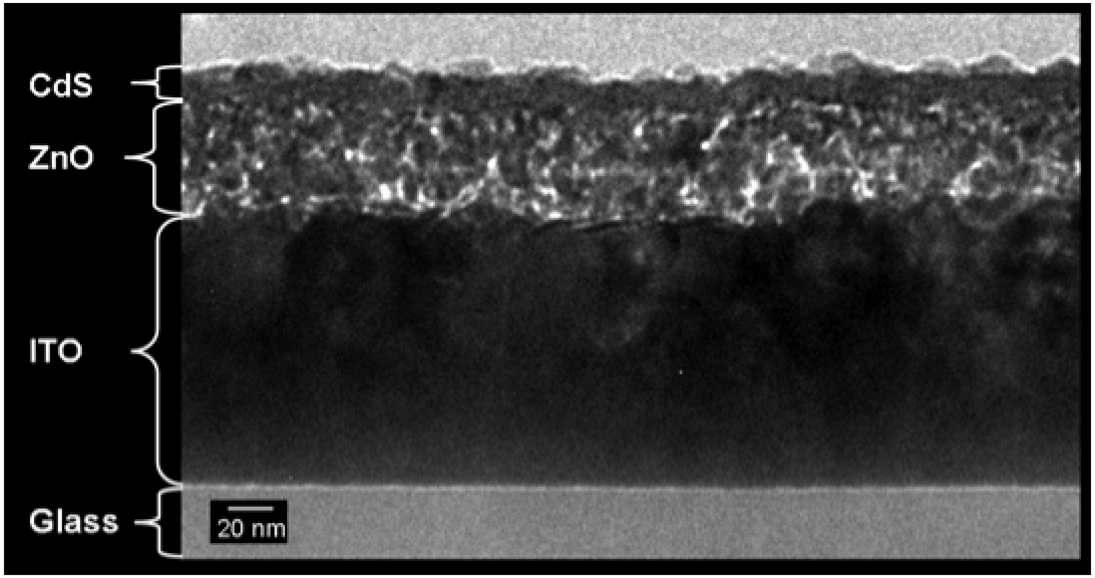
Can we use biomimetic mineralization strategies to control nanoscale CdS growth?

McCandless, et al. “Cadmium Telluride Solar Cells.” in *Handbook of Photovoltaic Science and Engineering*. Wiley, 2003.

# Nanocrystal Layer Deposition (NCLD) of CdS on ZnO

Room temperature, aqueous synthesis

$$CH_3C(S)NH_2 + Cd(OH)_2 \longrightarrow CH_3C(O)NH_2 + CdS + H_2O$$




NCLD grows a thin (~10-20 nm), dense film of CdS on ZnO surfaces.

Spoerke, et al. J. Phys. Chem. C. 113, 16329 (2009)

# The Mechanism of NCLD

## Why is CdS Selective for ZnO Surfaces?

At pH 5.5

- Very few cadmium hydroxide species
- ZnO will be heavily decorated with bridging hydroxyls

$$CH_3C(S)NH_2 + Cd(OH)_2 \longrightarrow CH_3C(O)NH_2 + CdS + H_2O$$

$$CH_3C(S)NH_2 + Zn(OH)_2 \longrightarrow CH_3C(O)NH_2 + ZnS + H_2O$$

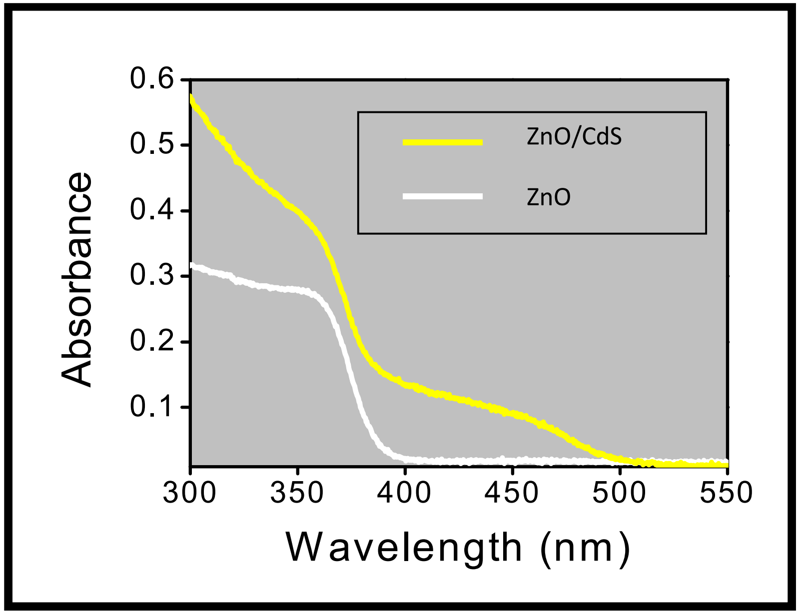
Hydroxylated ZnO will bind cadmium ions, forming $Cd(OH)_x$ complexes capable of nucleating CdS directly on ZnO surface.

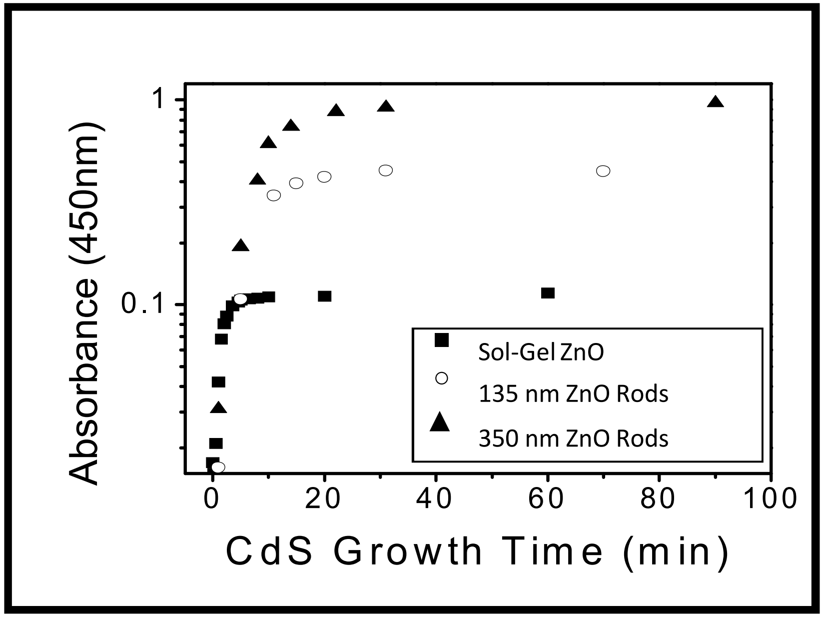
*1. Because the surface is the only source of $Cd(OH)_x$, the reaction will terminate over a surface densely covered with CdS.*

*2. Non-hydroxylated surface will not nucleate the CdS, producing selectivity.*

# Self-Limiting Growth

**UV-Vis absorption shows CdS absorption onset corresponding to ~2.4eV band gap.**

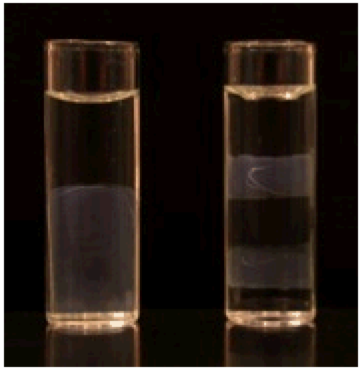



Monitoring CdS growth with absorbance shows that film formation is *self-limiting!*

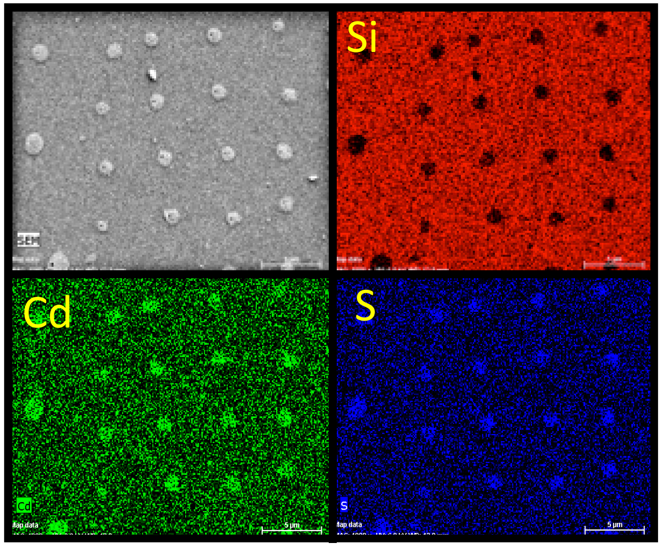
# Surface-Selective CdS Growth

CdS growth on ZnO is selective on both macro- and microscales

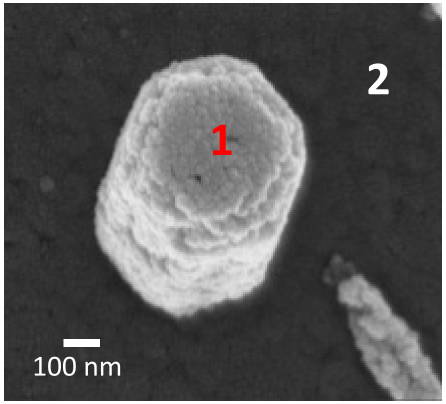


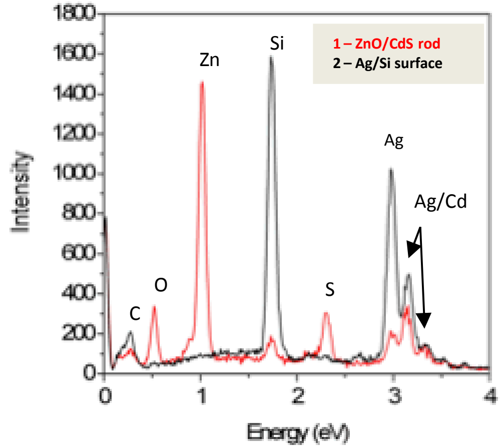
ZnO coated on glass slides at $t_0$ in CdS reaction solution.

CdS (yellow) selectively grown on ZnO-covered regions after 10 minutes growth.



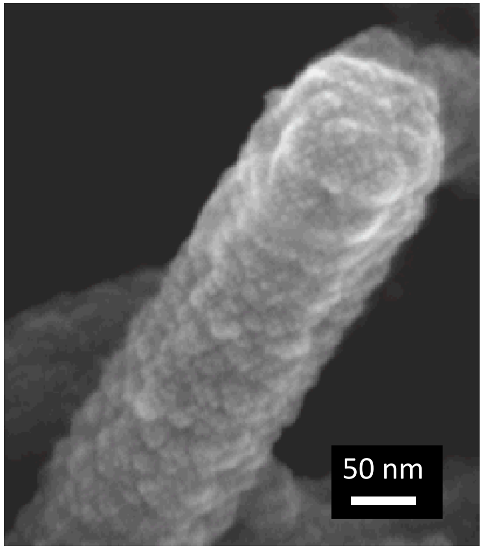

Stamped “micro-dots” of ZnO on Si produce selective CdS growth



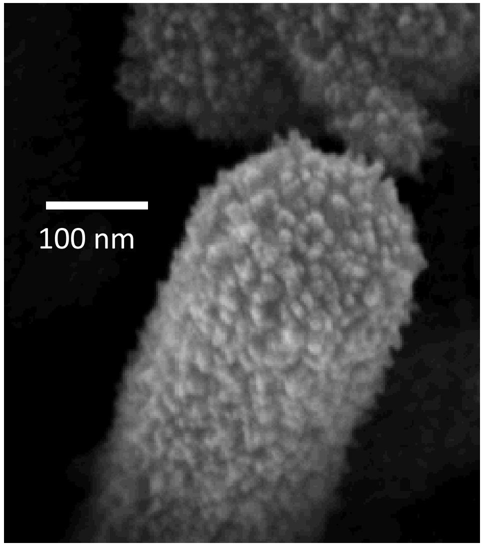



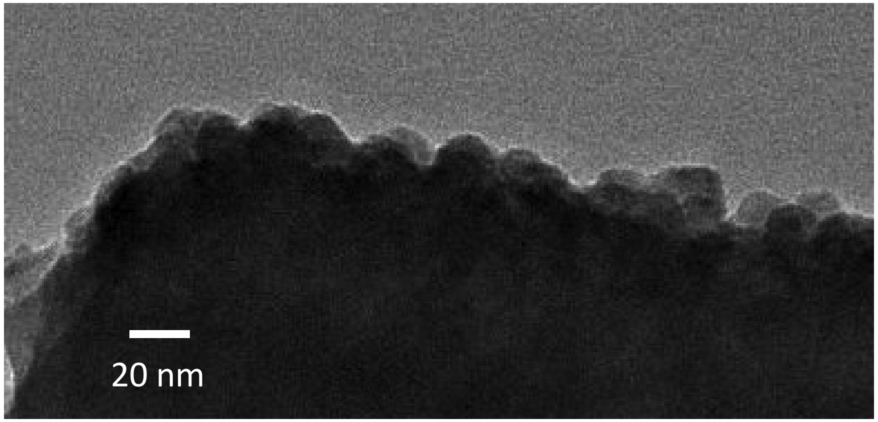

ZnO nanorods on Ag selectively template CdS

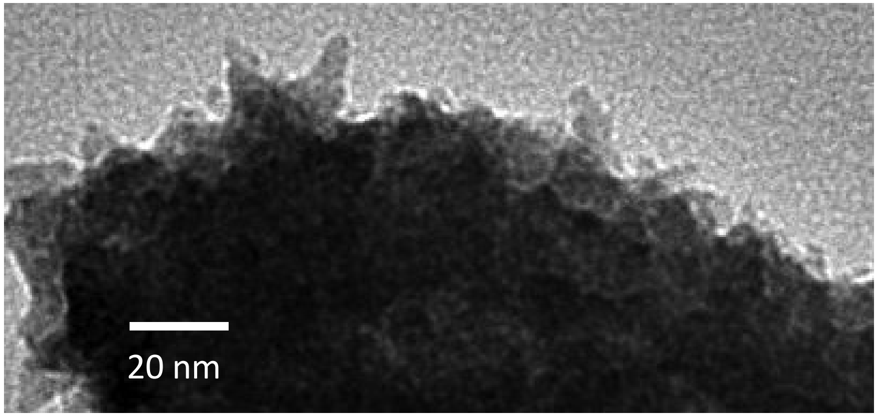
# Organic Crystal Growth Modifiers



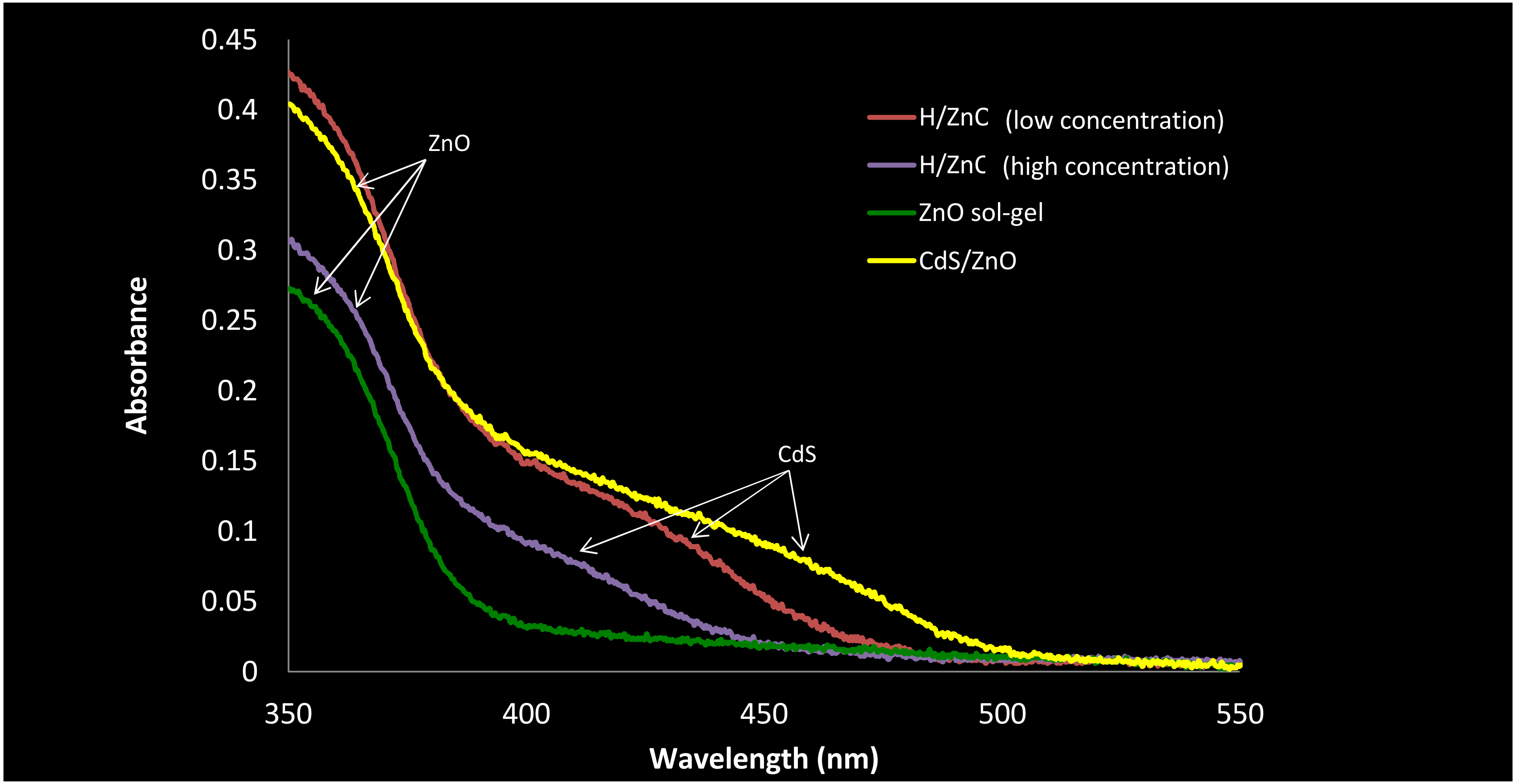

Introducing amino acids (e.g. histidine) to the crystal growth reaction dramatically changes the CdS nanocrystalline morphology.



# Histidine Influence on Optoelectronics

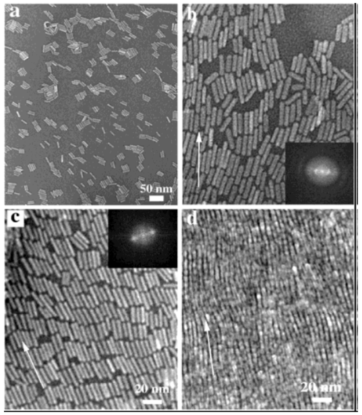



Incorporation of histidine into CdS growth results in a dramatic blue shift in absorbance. This effect reduces parasitic absorbance and $E_g$ increases by ~ 0.3 eV!

# Motivation to Use Biomaterials as Nano-Organizers

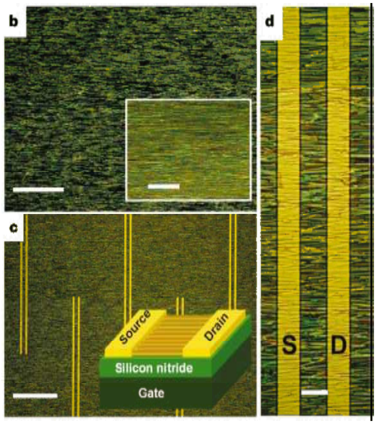
Controlled assembly of nanomaterials is an important challenge, limiting the widespread application of many materials.

Langmuir films



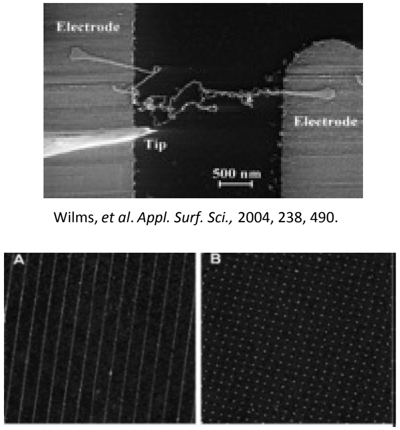

Kim, *et al*. *JACS,* **2001,** *123,* 4360.

Flow-based assembly




Duan, *et al*. *Nature*, 2003, 425

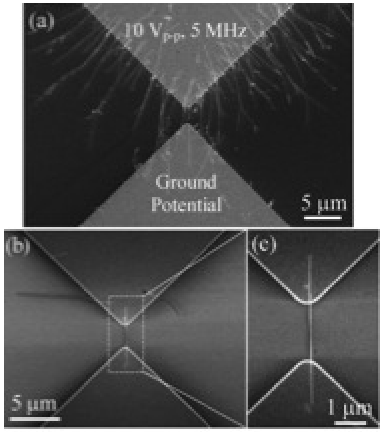
Nanomanipulation




Wilms, *et al*. *Appl. Surf. Sci.,* 2004, 238, 490.

Zhang, *et al*. *Adv.Mater*, 2002; 14, 1472.

Dielectrophoresis

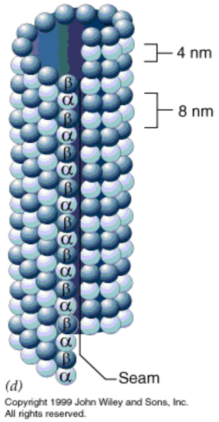



Dong, *et al*. *Nano Lett,* 2005, 5, 2112

## Our Approach:

Utilize dynamic materials such as microtubules and motor proteins to direct the synthesis, organization, and assembly of nanomaterials.

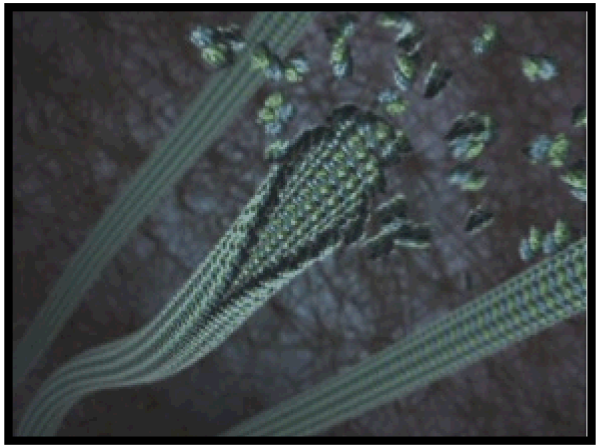
# What are Microtubules?




Polar protein filaments
(~25 nm diameter)

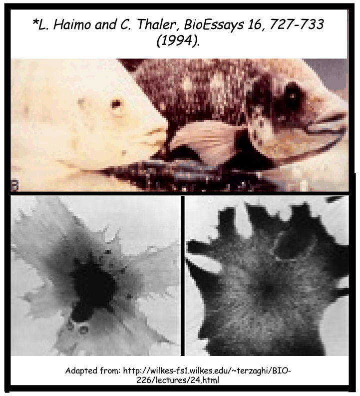
Polymerized from a-tubulin/b-tubulin dimers

Highly specific interactions with motor proteins (kinesins and dyneins)

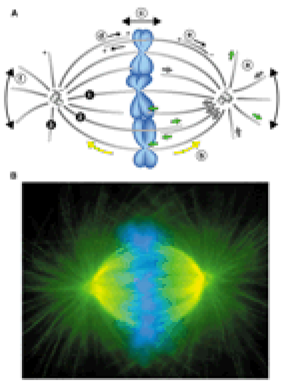


"Inner Life of the Cell," Harvard University

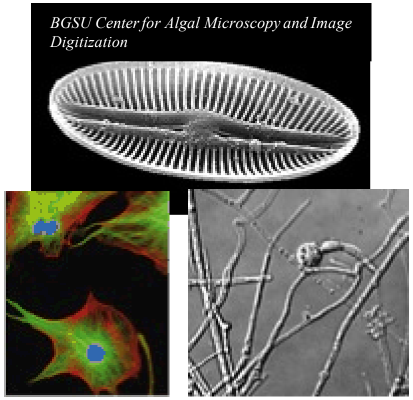
MTs facilitate intracellular organization across a wide range of natural systems.




Adaptive reorganization of pigment granules in melanophore cells



Chromosome positioning and separation during cell splitting

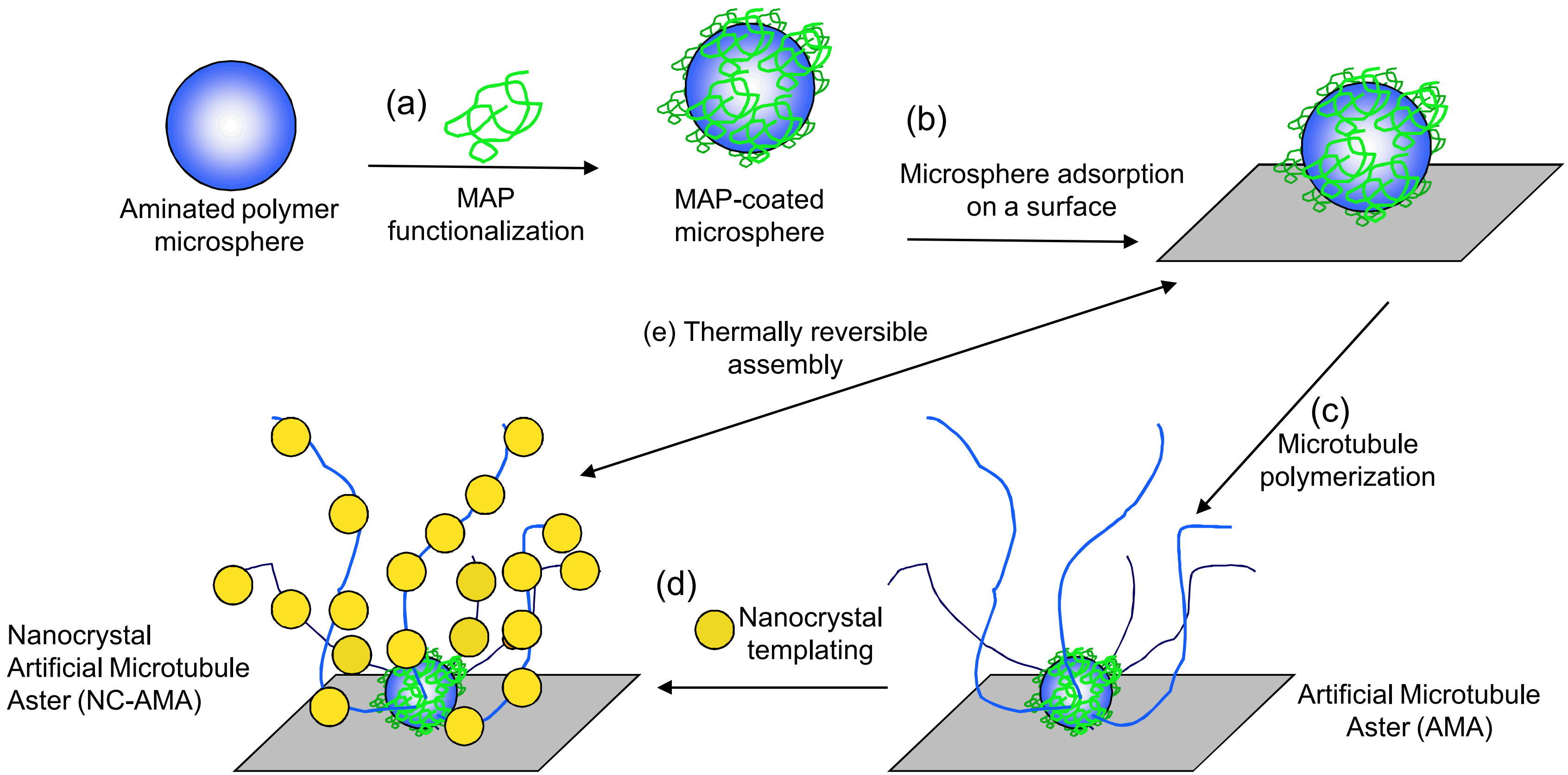



http://probes.invitrogen.com/

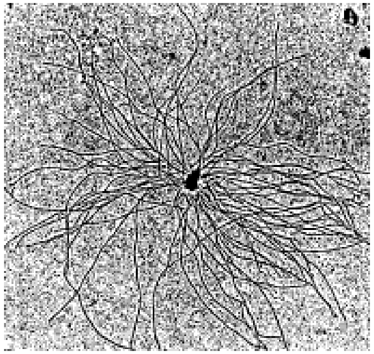
Trafficking of vesicles and macromolecule building blocks

Sandia National Laboratories

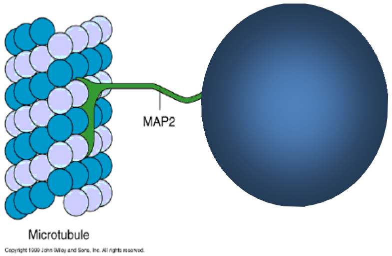
# Forming Microtubule Asters for 3D Templating of Nanocrystals

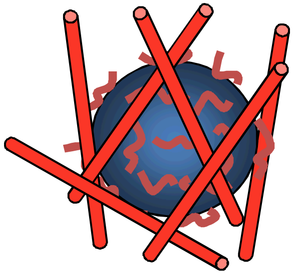


# MAP-mediated assembly of 3D MT Asters

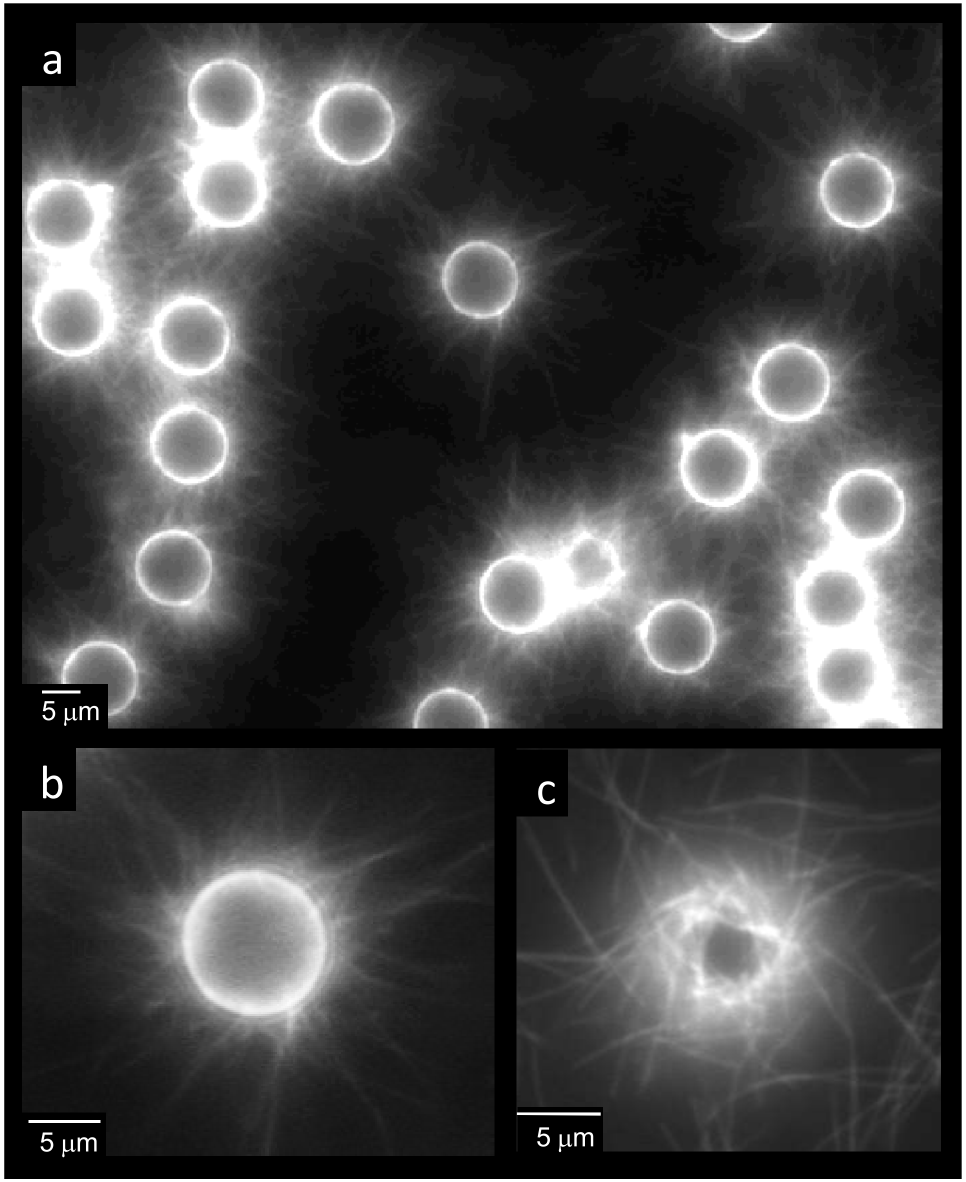


http://users.rcn.com/jkimball.ma.ultranet/BiologyPages/C/Cytoskeleton.html#centrosome

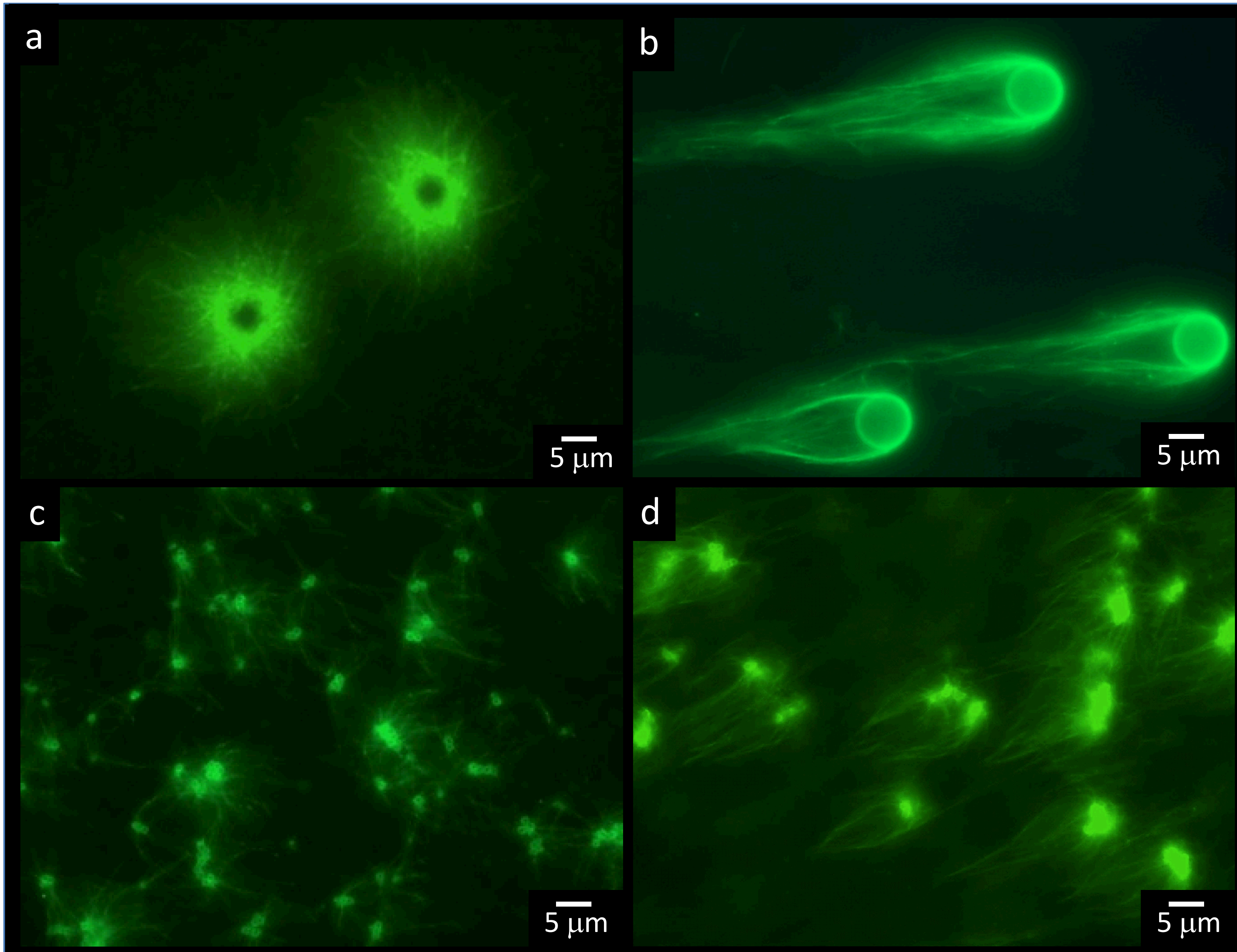


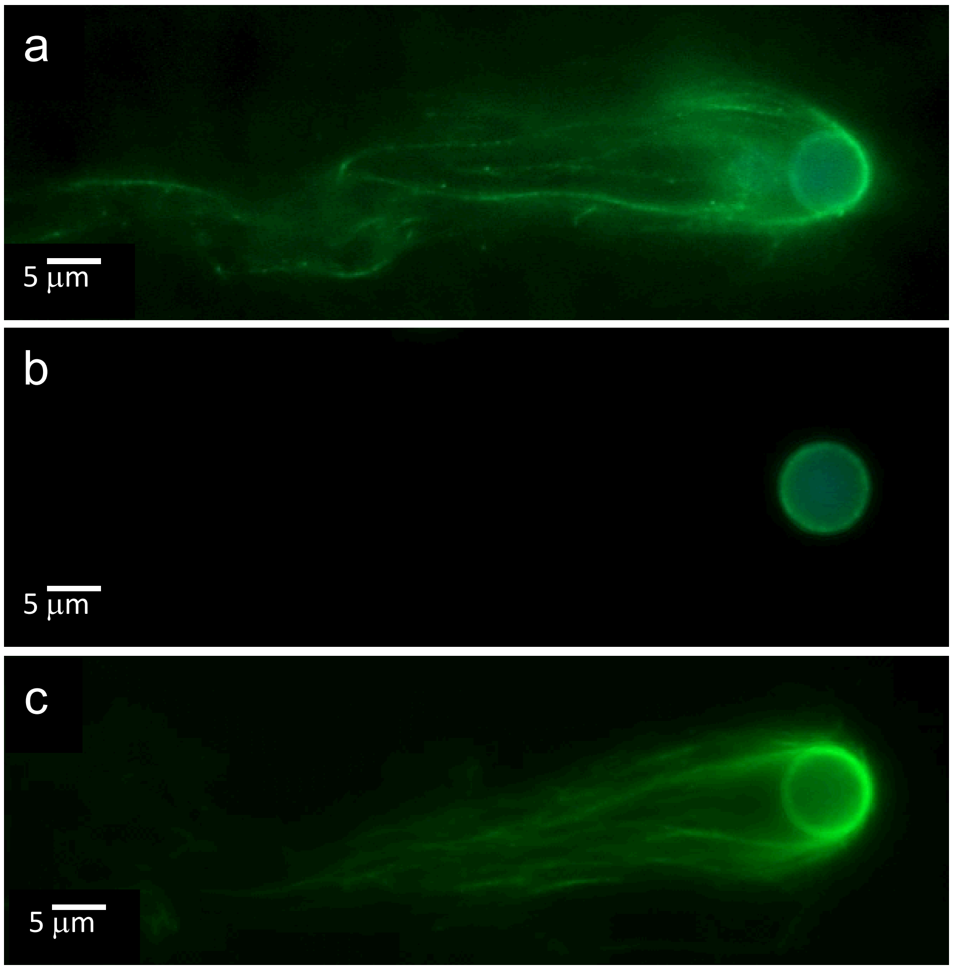
MAPs (1,2, Tau) serve to nucleate and stabilize the MT growth around a central particle.



# Templating Streptavidin Nanocrystals onto Biotinylated Asters



# Thermally Reversible Character of Aster-Nanocrystal Composites



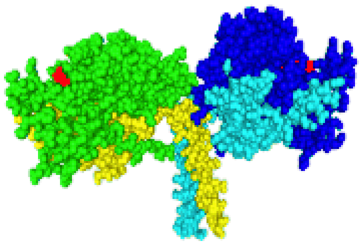

As made

4°C

Reconstituted (37°C)

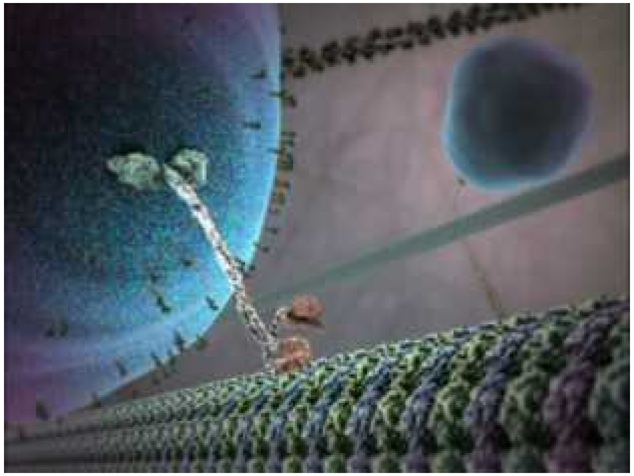
# Kinesin Motor Proteins and “Inverted Motility”

## Kinesin



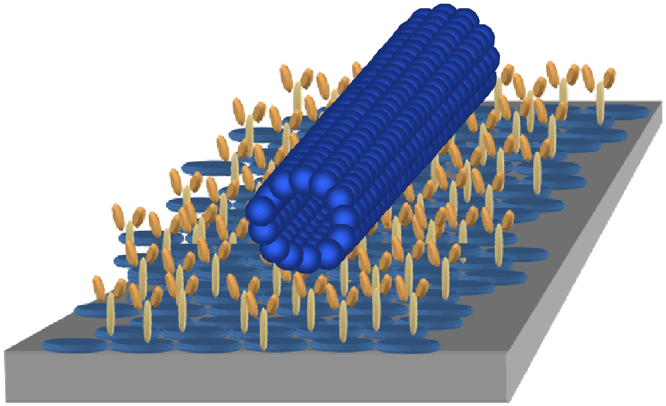
a mechanochemical protein (force-generating enzyme)

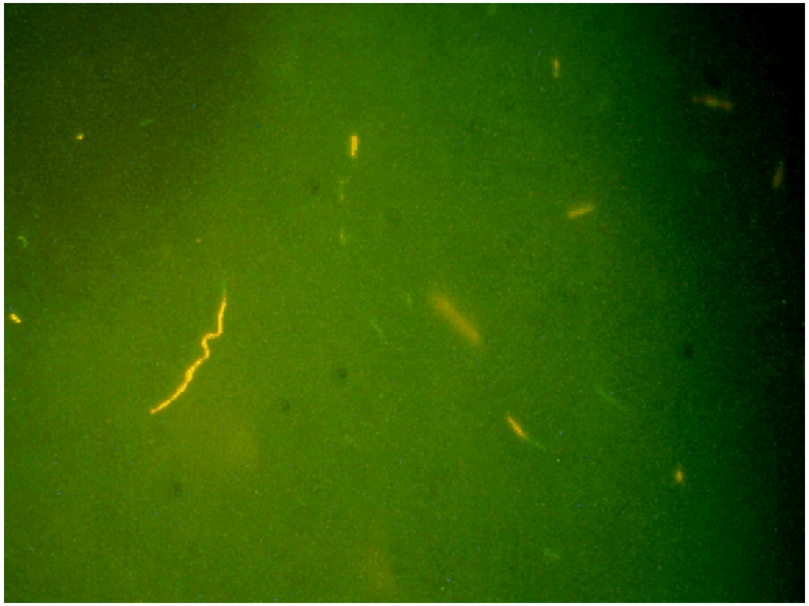
by binding and hydrolyzing ATP, kinesin latches onto MTs and translocates along them



“Inner Life of the Cell,” Harvard University

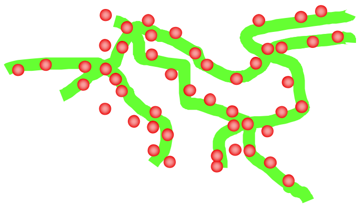
“Inverted Motility” utilizes an array of surface-bound inverted kinesins to transport microtubule shuttles over a surface



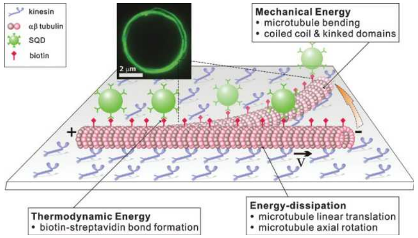


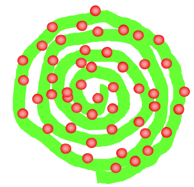
# Energy-driven, Active Assembly of Nanomaterials

Energy-driven transport can be used to assemble nanocomposite materials:
chemical energy → mechanical work → active assembly

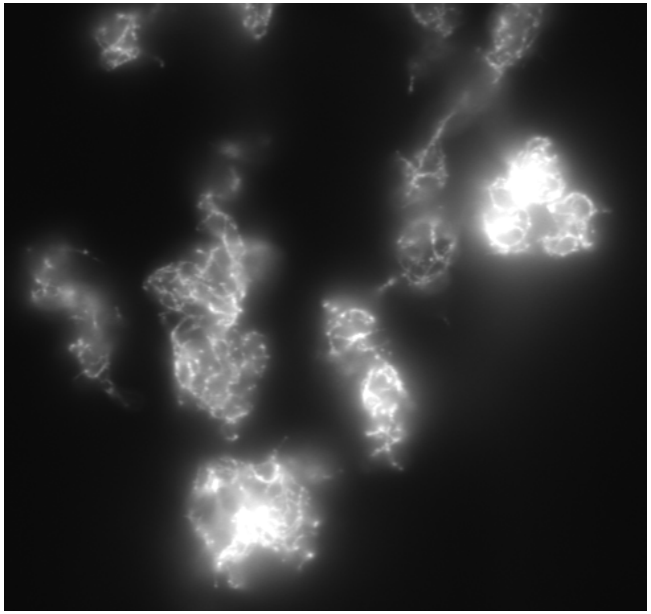


**QDs + biotinylated MTs**



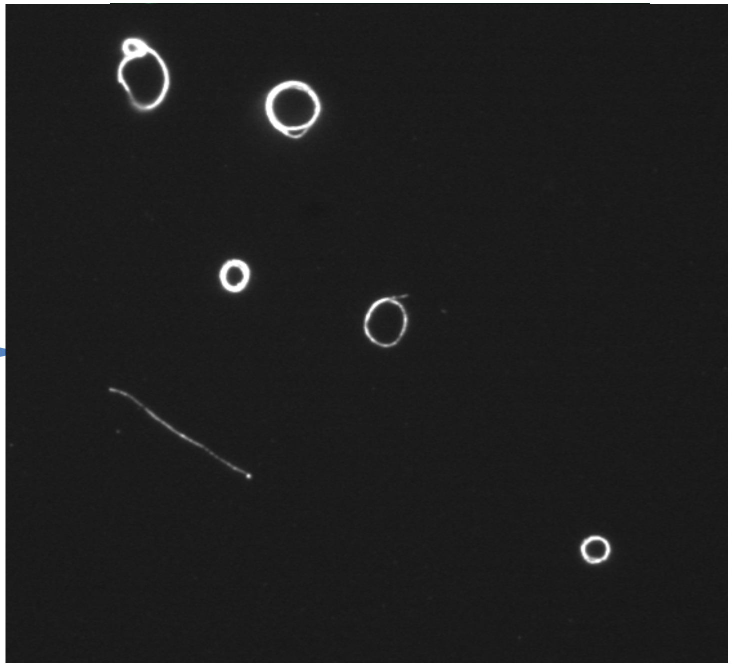
**QDs + gliding biotinylated MTs**



**Randomly assembled MTs and QDs (equilibrium)**

**Energy input via ATP hydrolysis**

**~50 kJ/mol ATP**

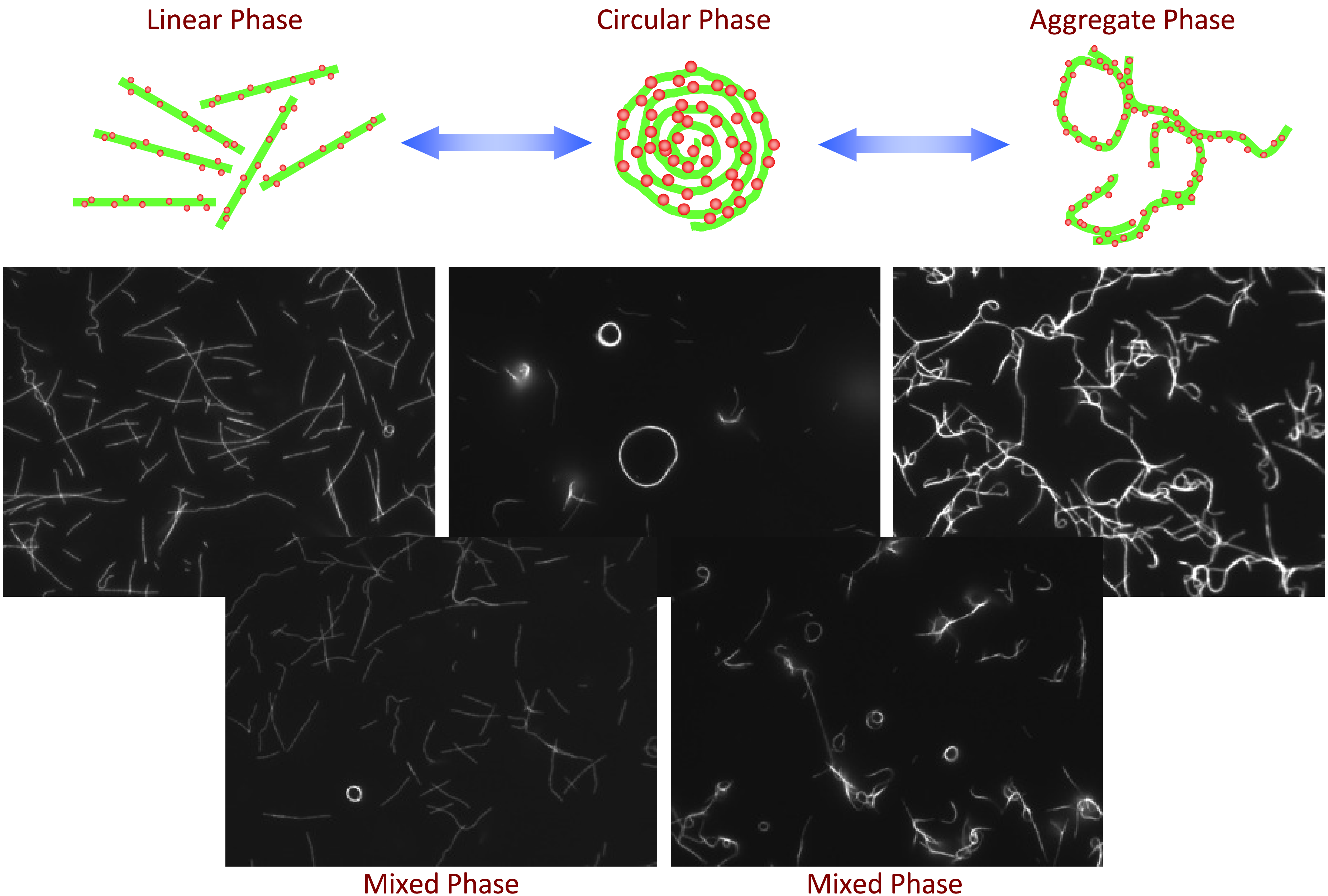


**Actively assembled MTs and QDs (+ energy)**

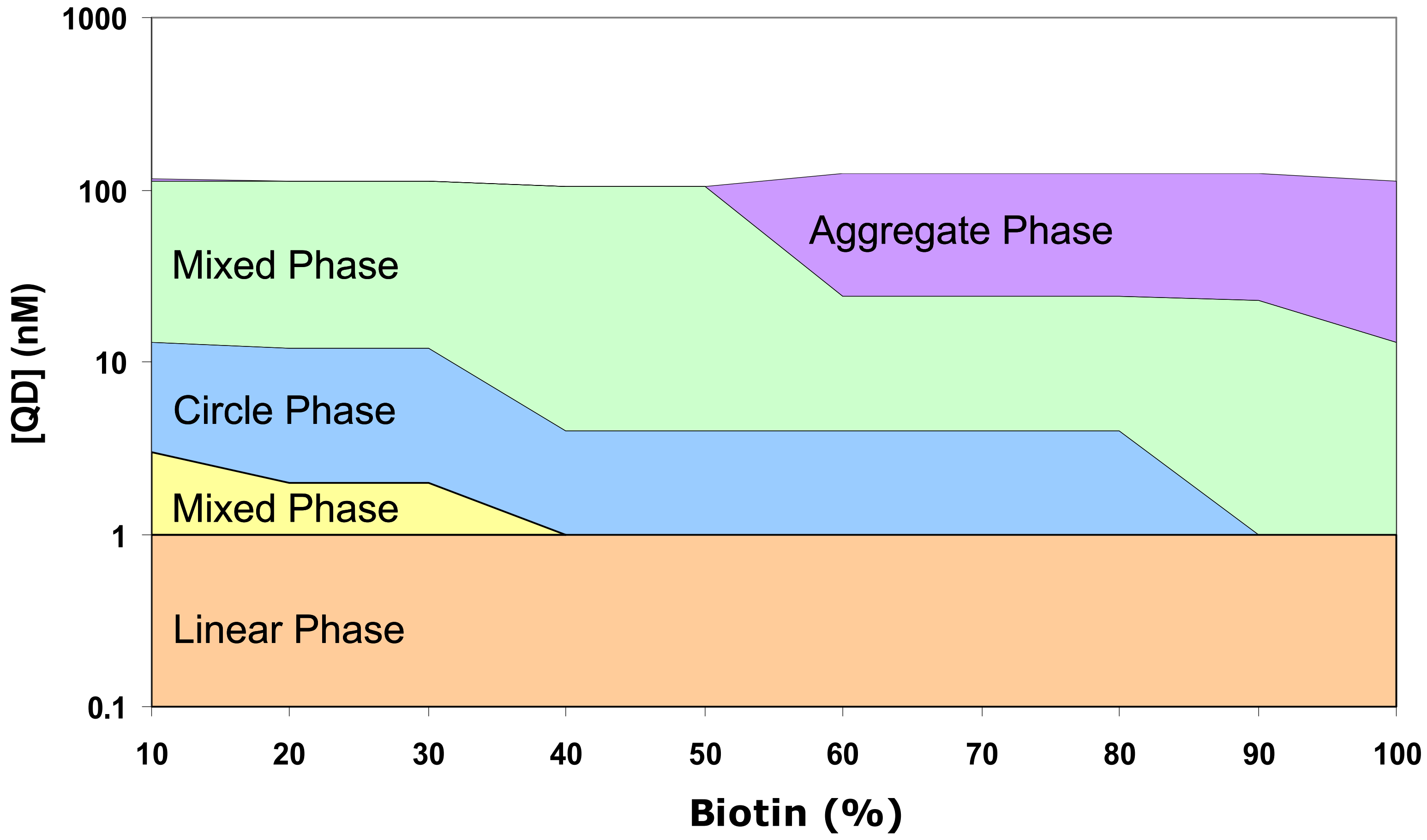
Bachand et al., *J. Nanosci. Nanotechol.*, **5**, 718 (2005)
Hess et al. *Nano Letters*, **5**, 629 (2005).

George Bachand, Marlene Bachand, Haiqing Liu

# Active Assembly – Phase Transitions



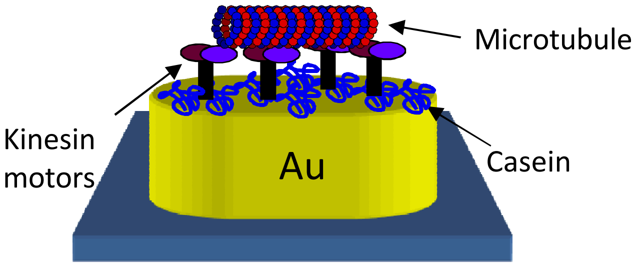
# Phase Diagram of Ring Assembly

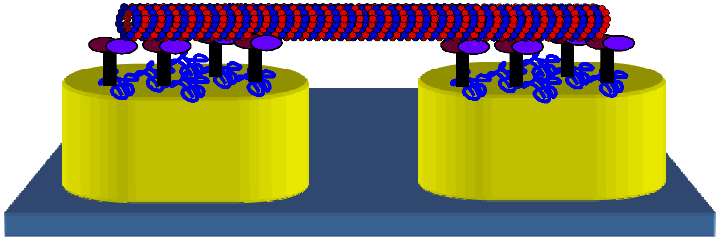


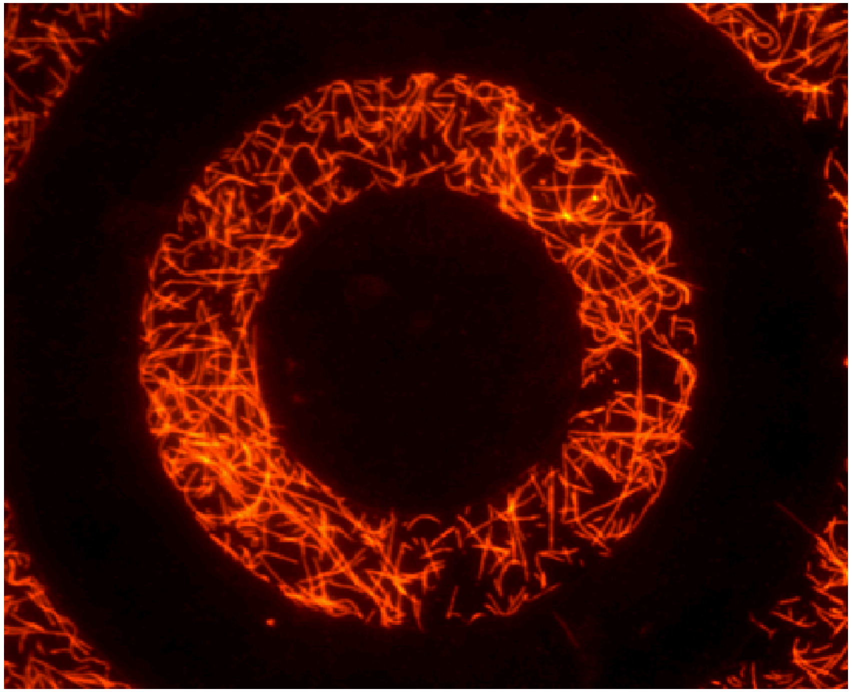

A simple phase diagram can be constructed to describe the conditions necessary to achieve the assembly of circular nanocomposites.

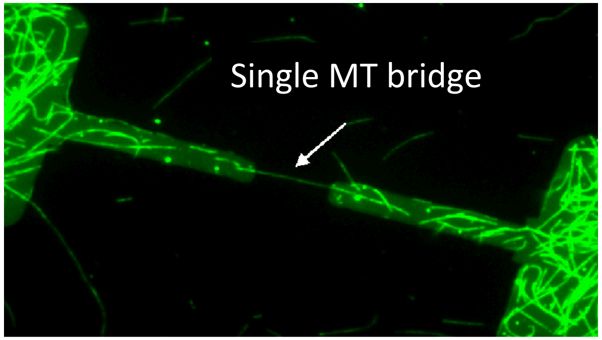
# Selective MT Capture

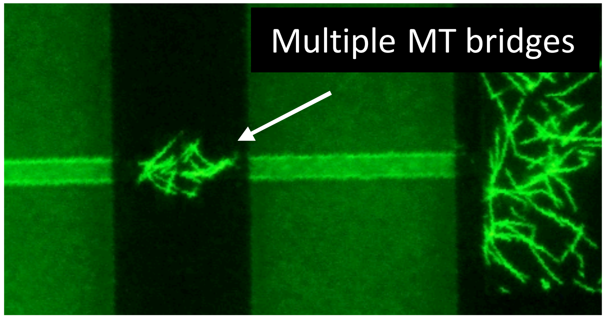
*When ATP is replaced with AMPPNP, kinesins bind MTs statically*



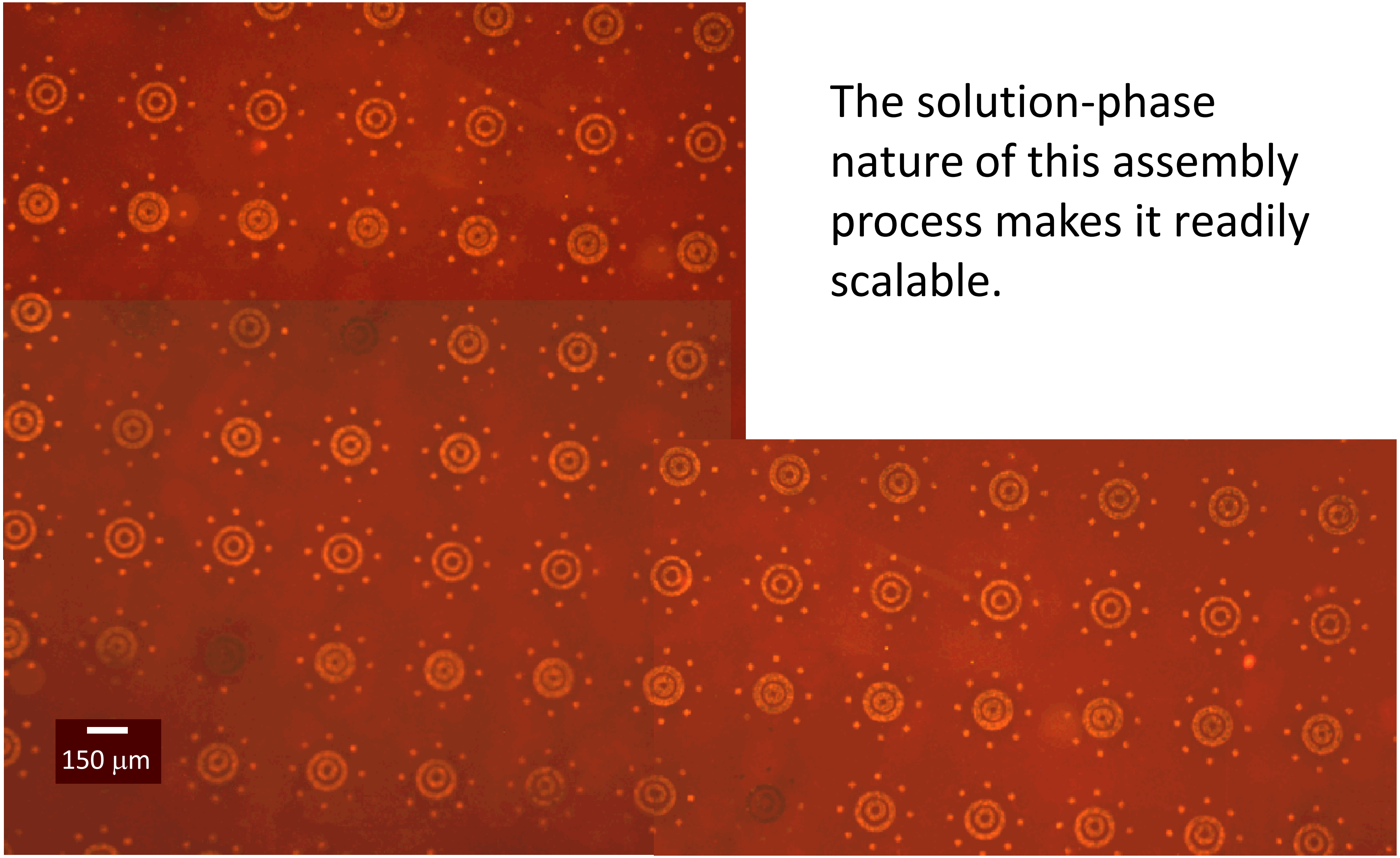







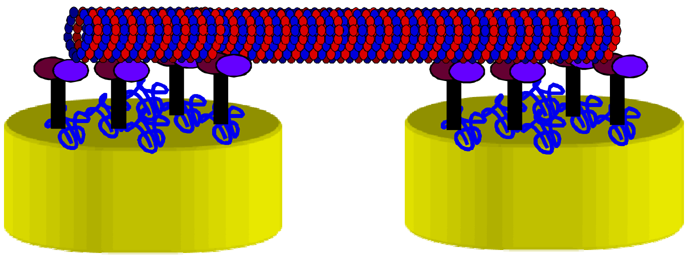



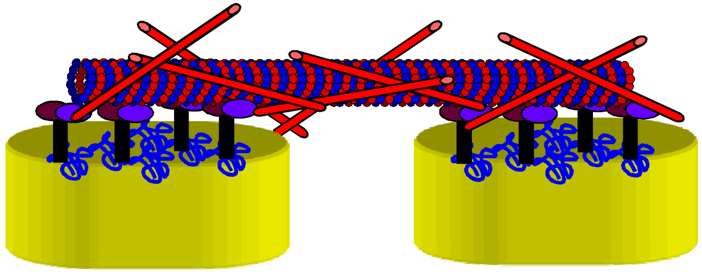
# Scalable Assembly

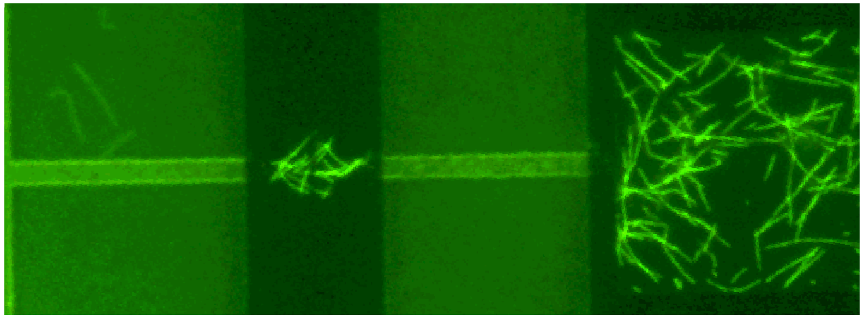


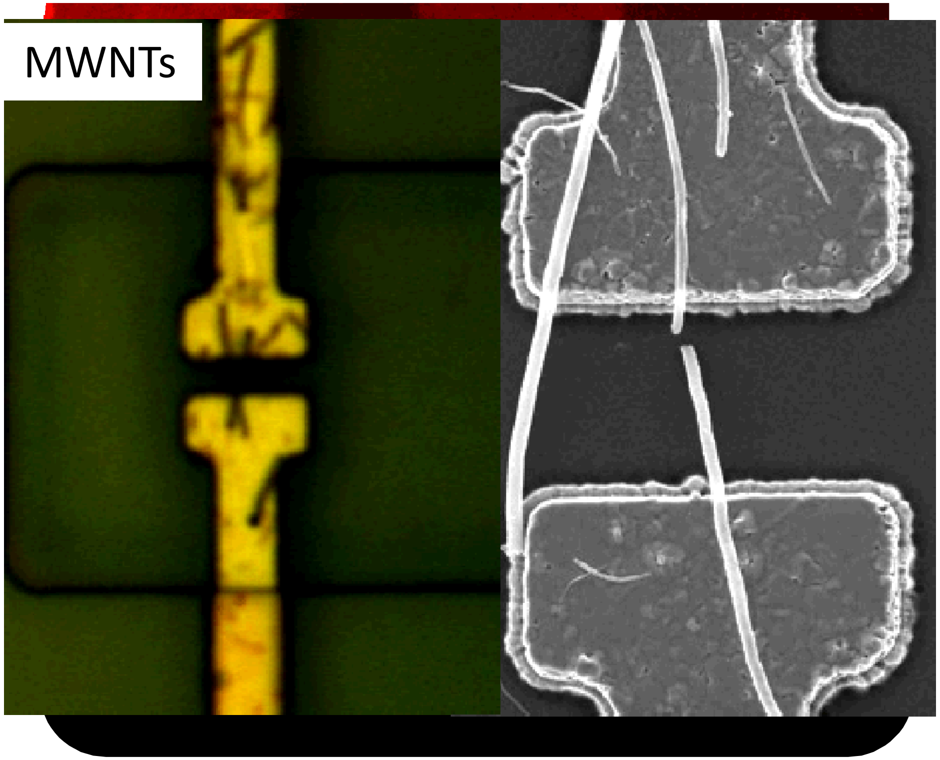

The solution-phase nature of this assembly process makes it readily scalable.

# Functional Nanomaterials Templating





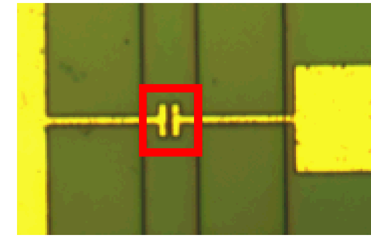


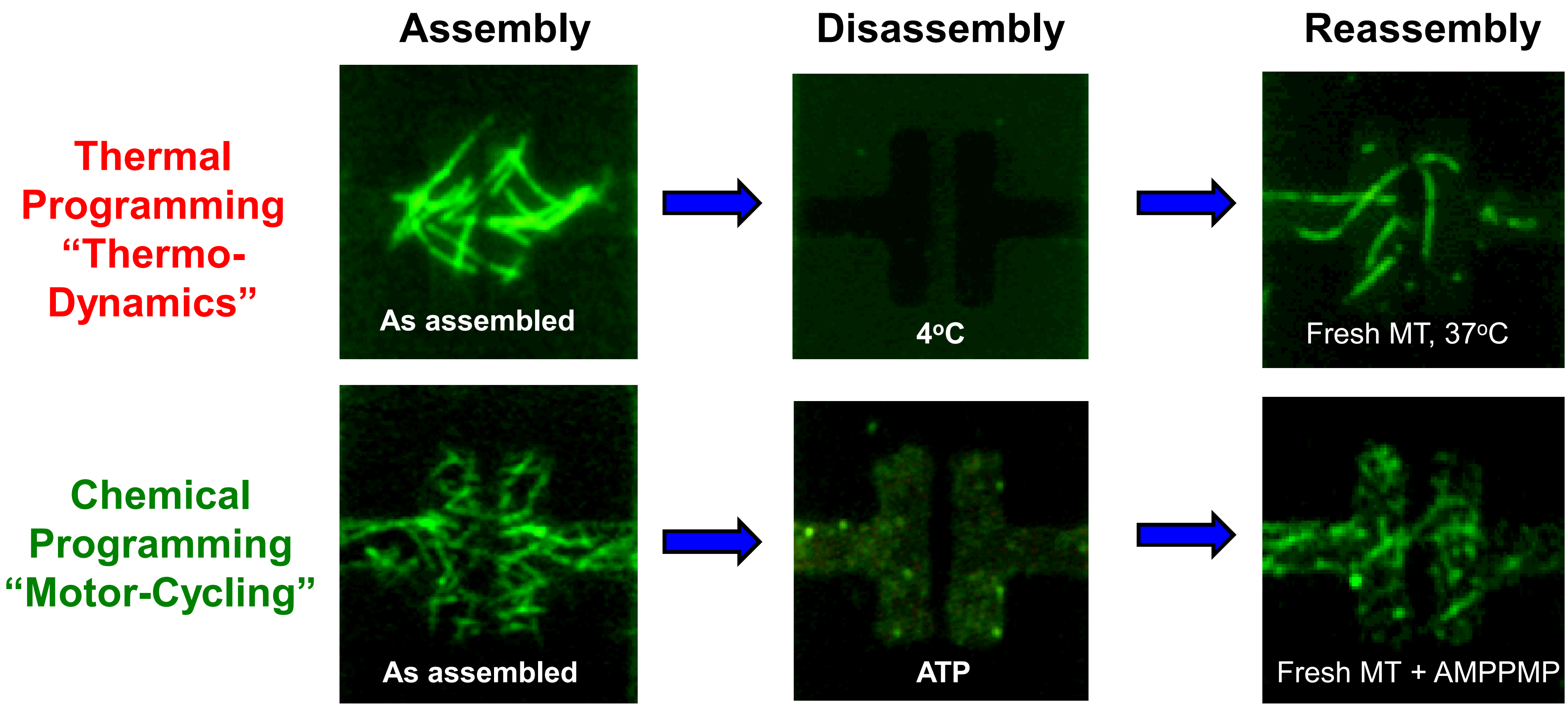



Kinesin-captured MTs will selectively bind to gold platforms, forming bridges between gold electrodes

# Programmable Character of Interconnect Assembly

Using the dynamic character of the MTs and the MT-kinesin interactions, we can program the reversible assembly of these interconnects.



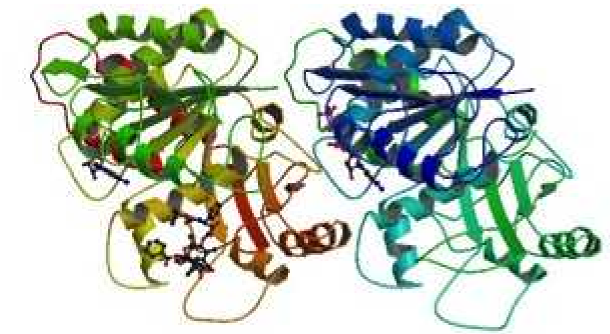


# Biotemplating with Microtubules…Why Microtubules?

- These organized, protein nanofilaments are extremely attractive biotemplates:

- Diverse chemistry makes them capable of interacting with a wide range of biomineral precursors

  Positive charges: Lysines, Arginines
  Negative charges: Glutamic acid, aspartic acid
  Chelators: Histidine (e.g. Fe)
  Thiol chemistry: Cysteines



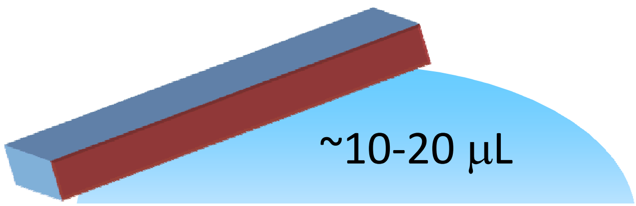
- They exhibit monodispersity in diameter around 25 nm.

- They can be assembled and organized on the nanoscale.

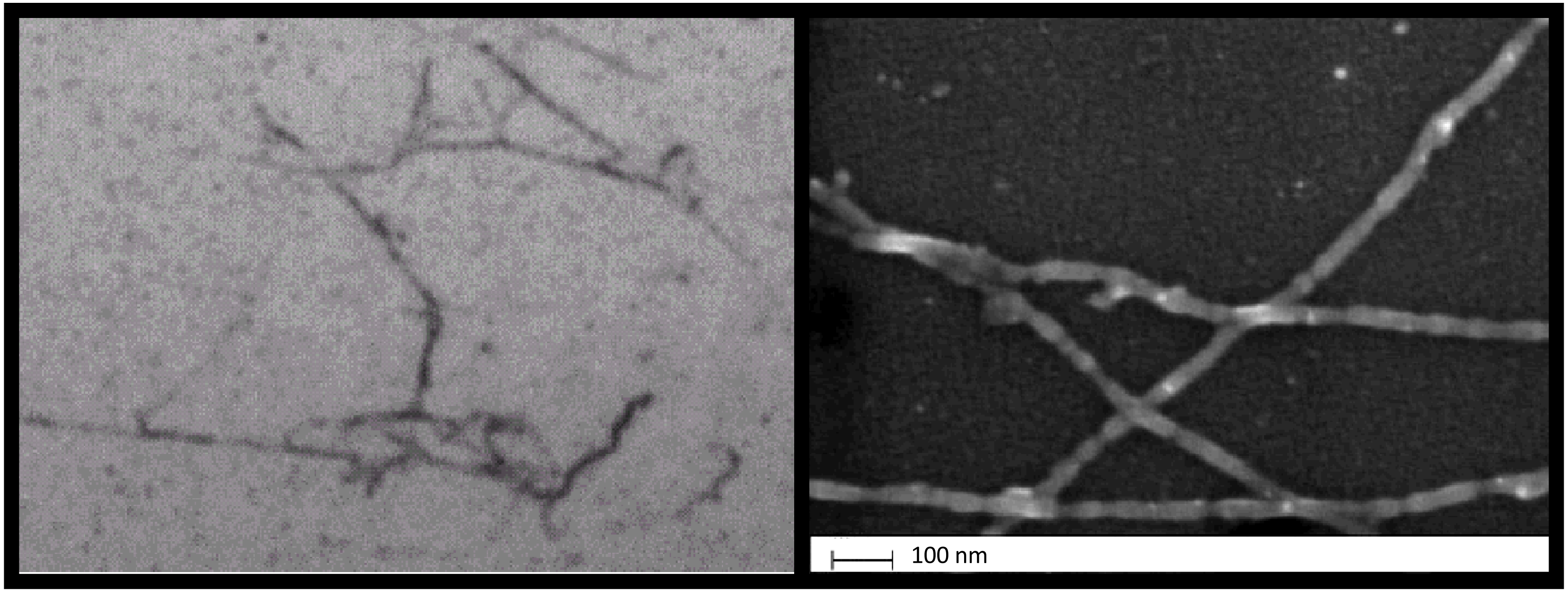
- MT chemistry and assembly can be manipulated for complex templating.

# Initial Demonstrations: Metallization

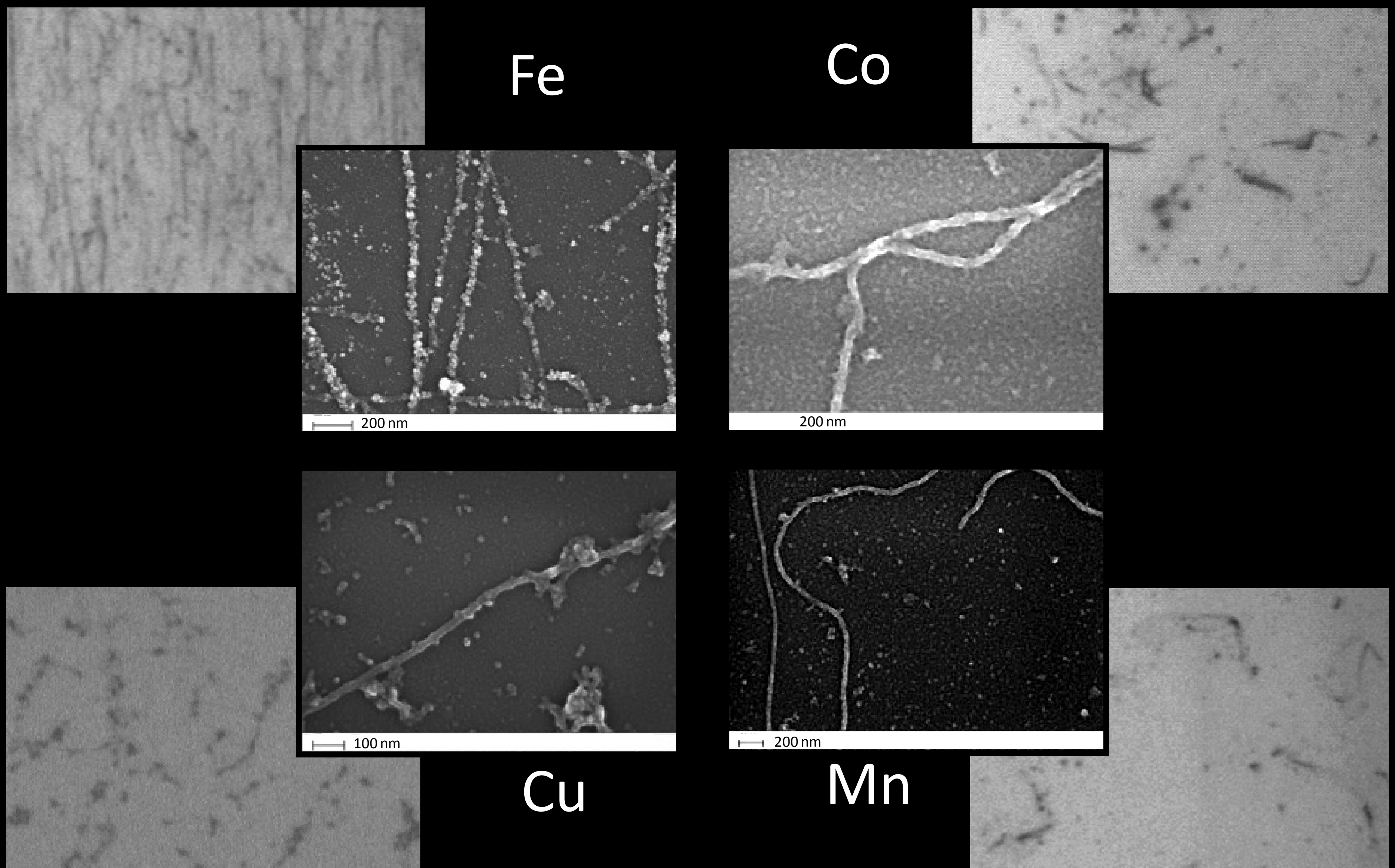
1. Microtubules (MTs) are bound to aminosilane-coated silicon substrates.
2. MTs are incubated in aqueous ionic solutions.
3. Reducing or oxidizing agents added to incubation solution to drive mineralization.




Metallization of microtubules with silver (Ag)



# Metallization Diversity



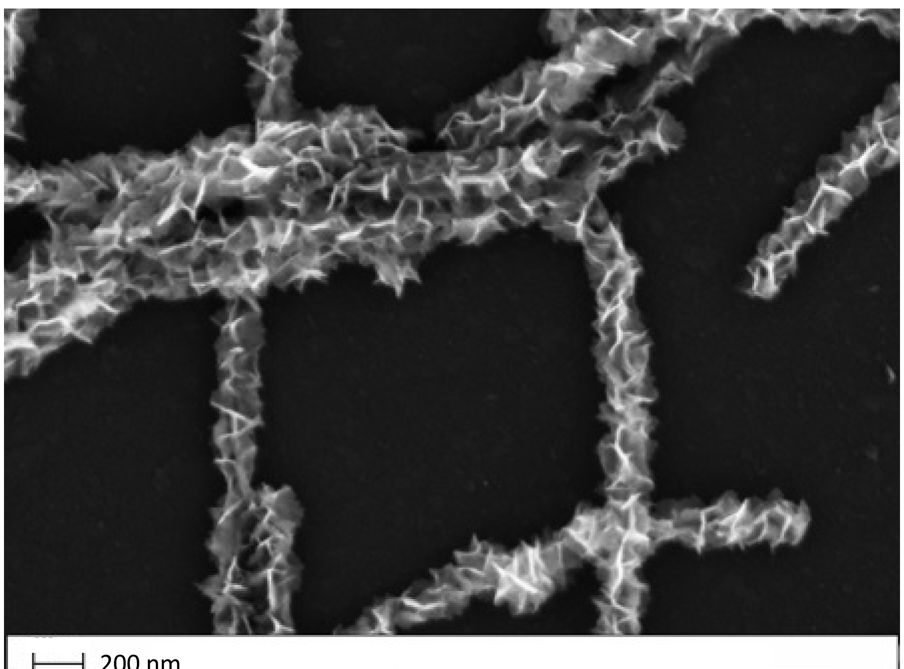
# Microtubule Mineralization

*In addition to metallization, MTs can serve as templates for mineralization*

## Iron oxyhydroxide (lepidocrocite)

1. Incubate unlabeled MTs in $Fe^{2+}$
2. Expose to $NH_4OH$ vapors

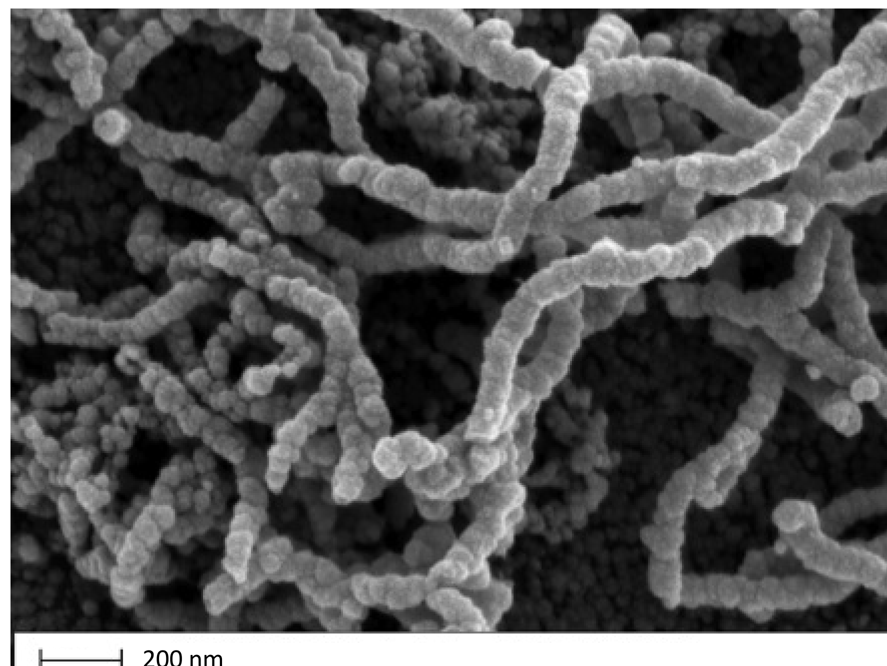
$$4Fe(OH)_2 + 4OH^- + O_2 \rightarrow 4FeOOH + H_2O + 2O^{2-}$$




## Cadmium sulfide

1. Incubate unlabeled MTs in 10mM Cd
2. Add equimolar thioacetamide
3. Expose to $NH_4OH$ vapors

$$Cd(OH)_2 + CH_3C(S)NH_2 \rightarrow CdS + CH_3C(O)NH_2 + H_2O$$



# Templating Mixed Materials

## Au/Ag

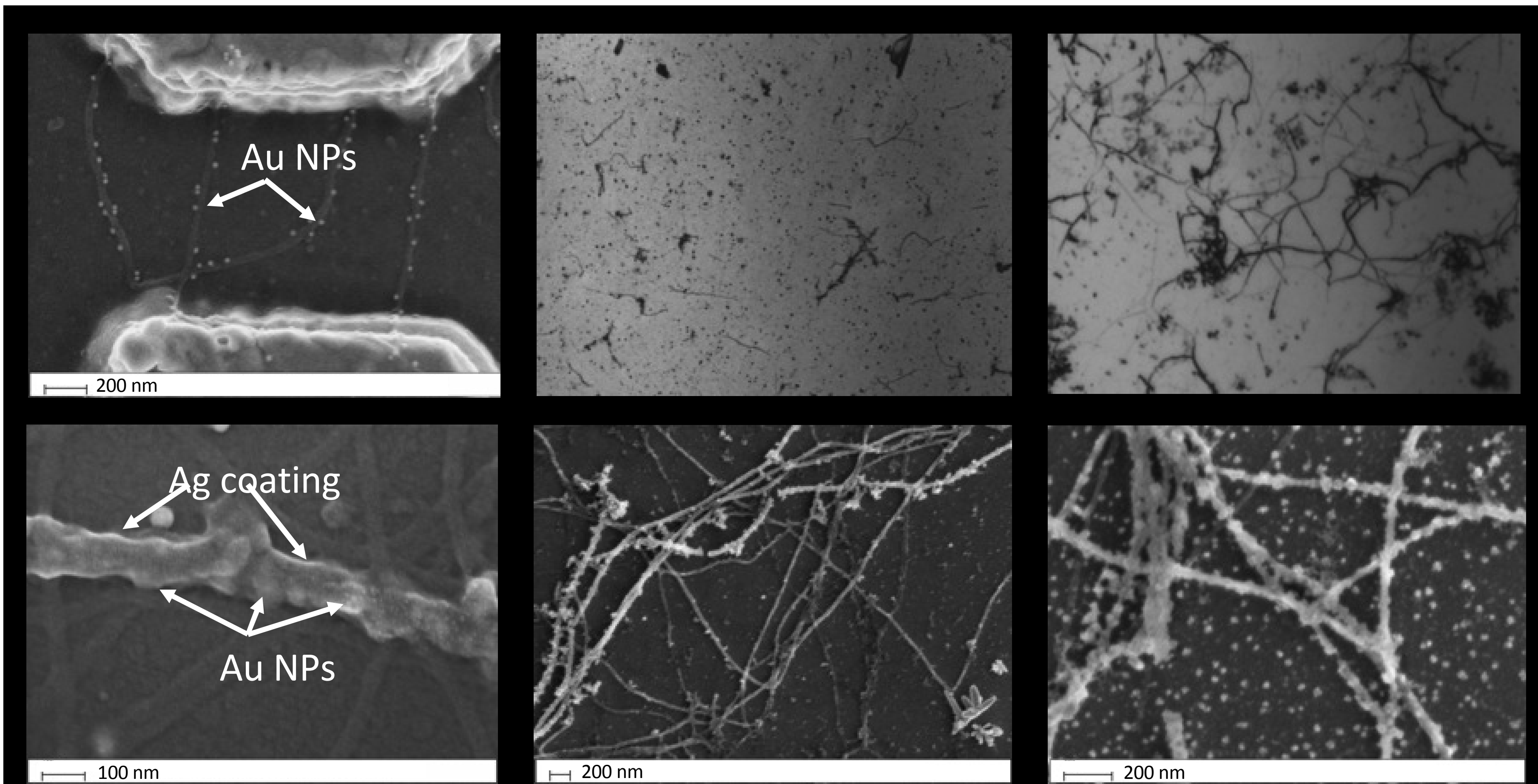
1. Treat biotinylated MTs with anti-biotin Au
2. Incubate with $Ag^+$
3. Reduce with hydroquinone

## Ag/FeOOH

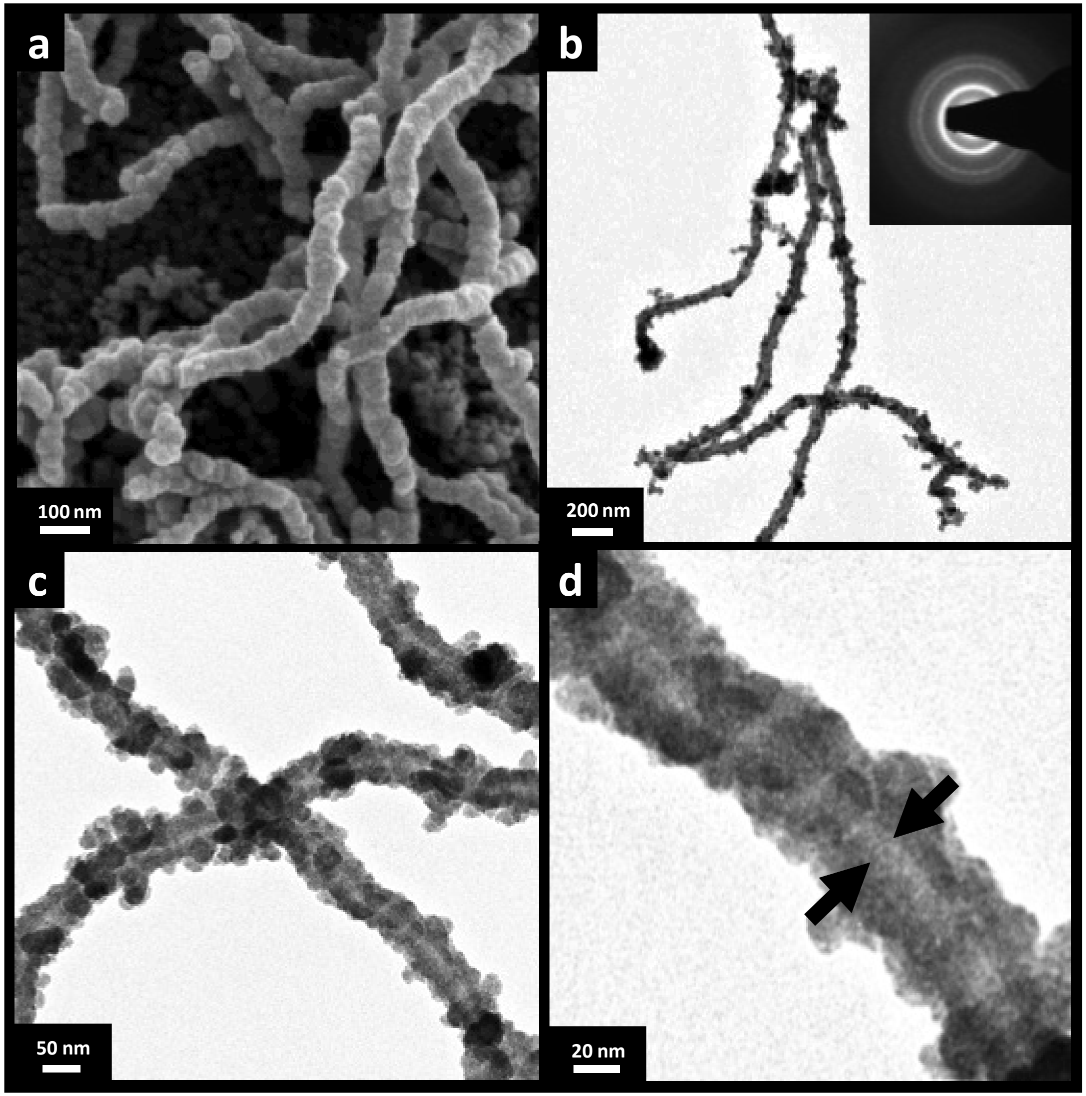
1. Incubate unlabeled MTs with $Ag^+$ and $Fe^{2+}$
2. Reduce with hydroquinone
3. Oxidize with $NH_4OH$ vapor

## Ag/$Mn_2O_3$

1. Incubate unlabeled MTs with $Ag^+$ and $MnO_4^-$
2. Reduce with hydroquinone



# A Closer Look at MT-Templated CdS



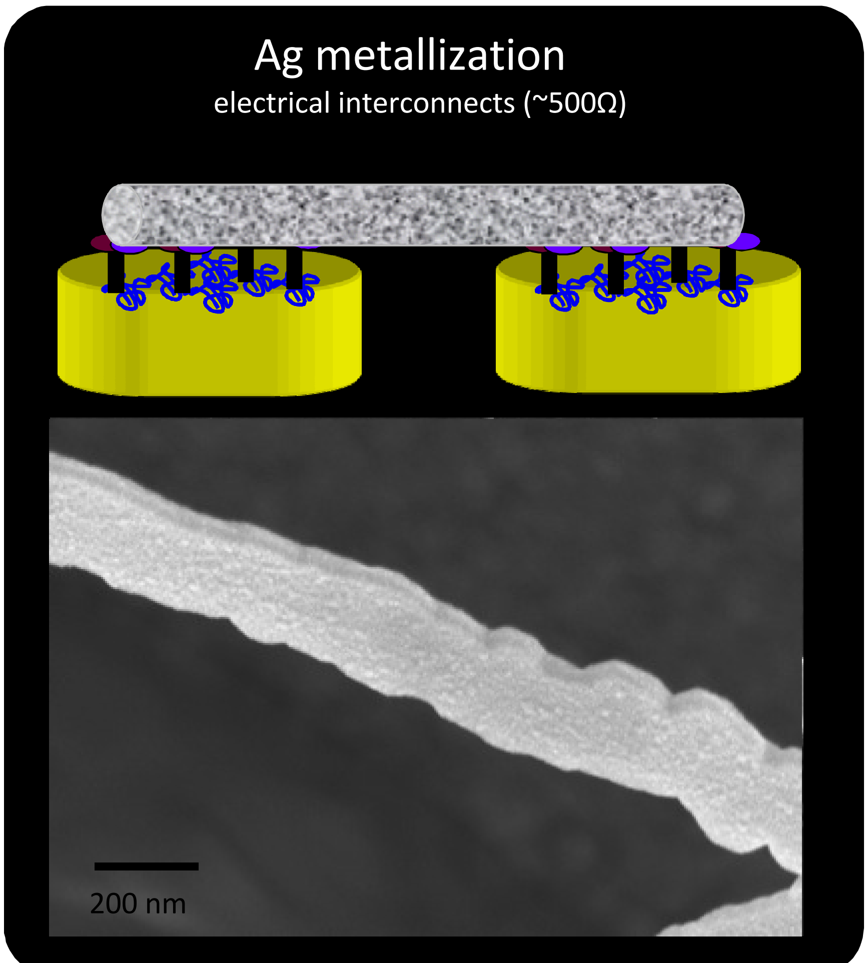

MT surface chemistry promotes dense, conformal *cubic* CdS mineralization, only a single nanocrystal thick.

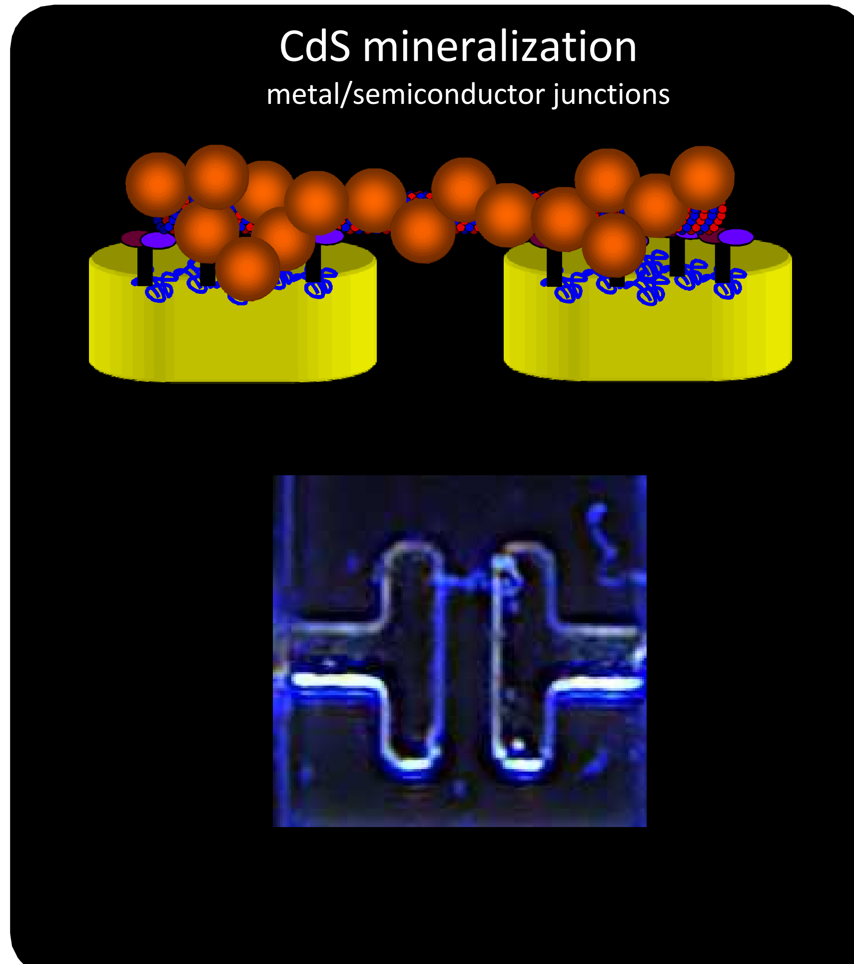
Mineralization is limited to the “bulk” of the protein assemblies – the central pore of the MT is preserved during CdS growth.

# Biotemplating Interconnects

MT bridges bind $Ag^{+}$ (left) or $Cd^{2+}$ (right) from aqueous solution

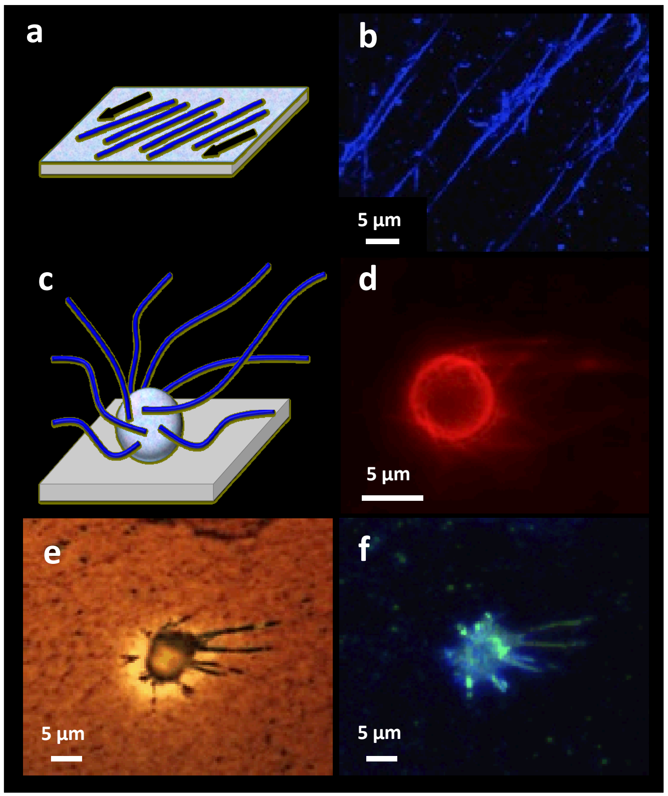
Subsequent treatment with either hydroquinone (for silver) or sodium sulfide (CdS) transforms MTs into functional interconnects



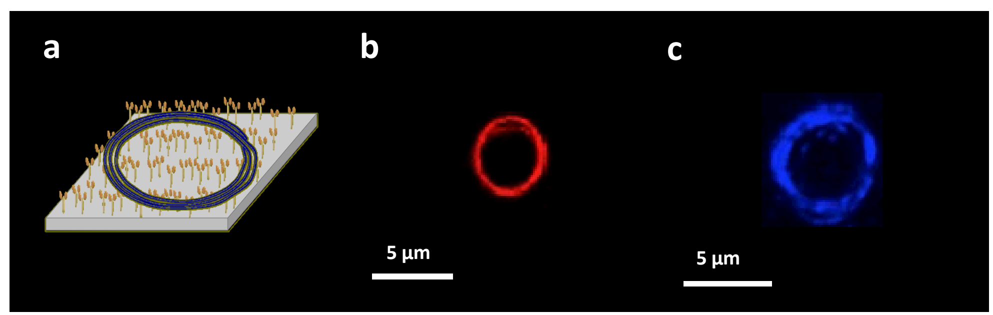



# Templating Bio-Mediated Morphologies

*Can the techniques applied to interconnects be applied to other structures?*

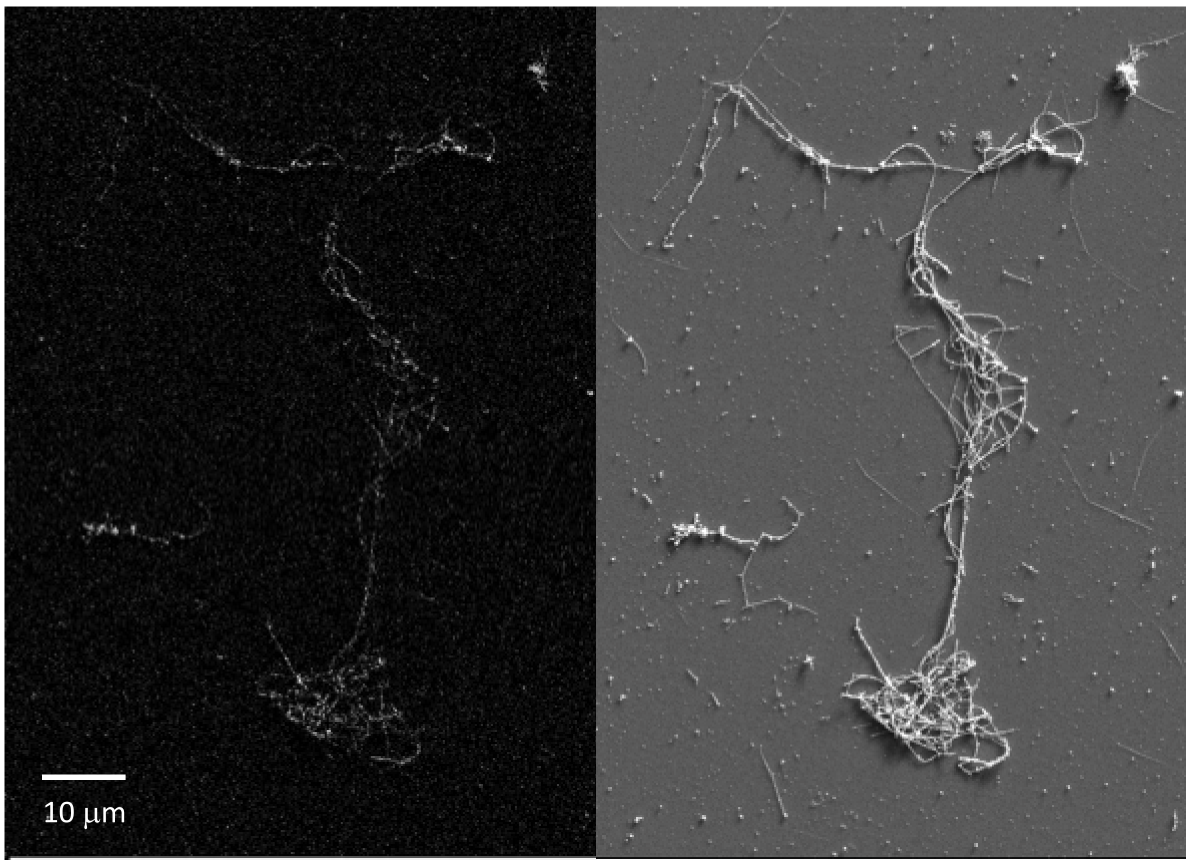



The biological character of MTs allows us to template the growth of unique, non-equilibrium CdS nanostructures



# Templating Luminescent Nanostructures

Templating *CdS* not only provides unique architectures, but creates functional (luminescent) structures.




Cathodoluminescent (left ) and scanning electron (right) images of CdS-coated MTs

# Thanks


## Funding Support

SNL Laboratory Directed Research and Development Program

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

NATIONAL INSTITUTE FOR NANO ENGINEERING NINE

U.S. DEPARTMENT OF ENERGY

**Office of Basic Energy Sciences**
**Division of Materials Sciences and Engineering**

U.S. DEPARTMENT OF ENERGY Energy Efficiency & Renewable Energy

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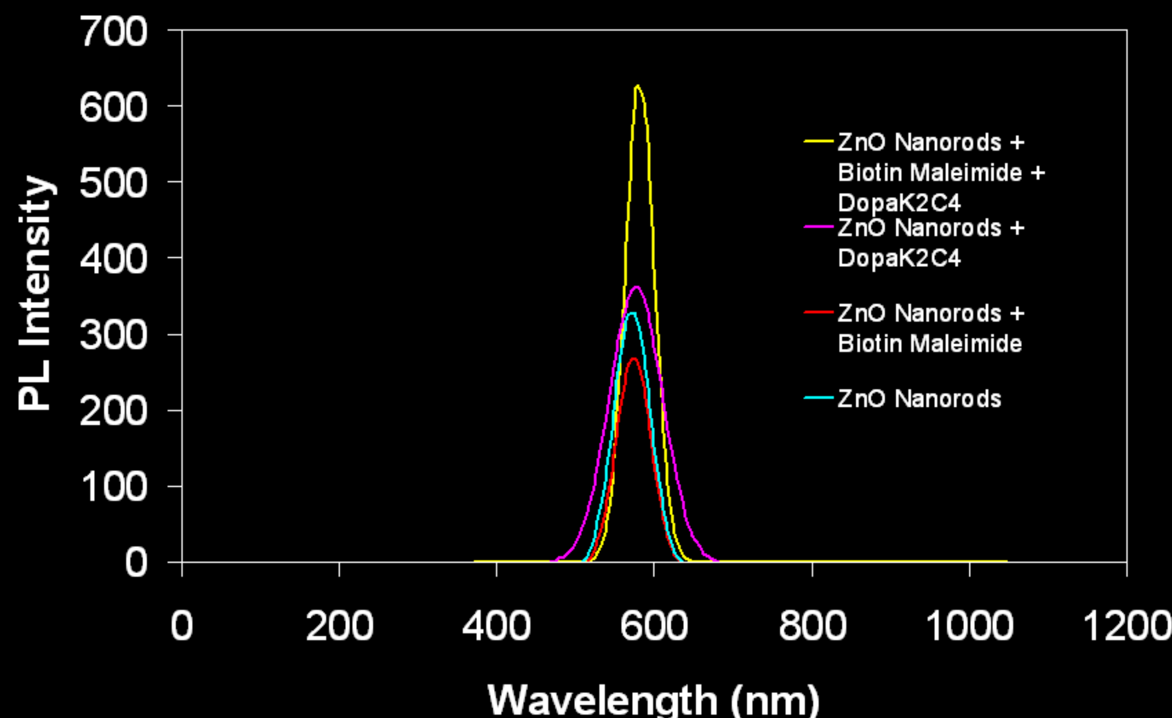
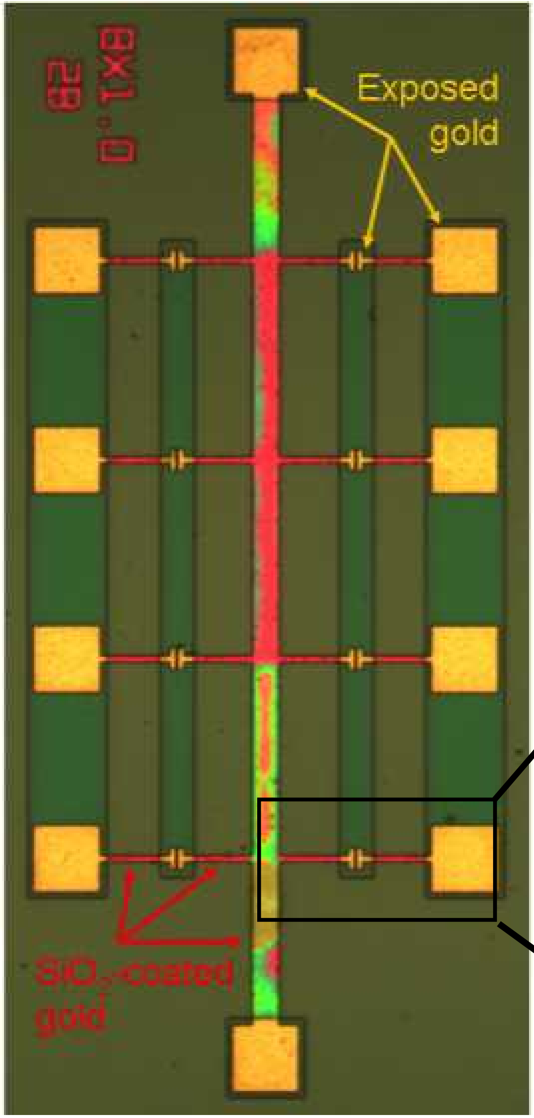
# Bonus Slides

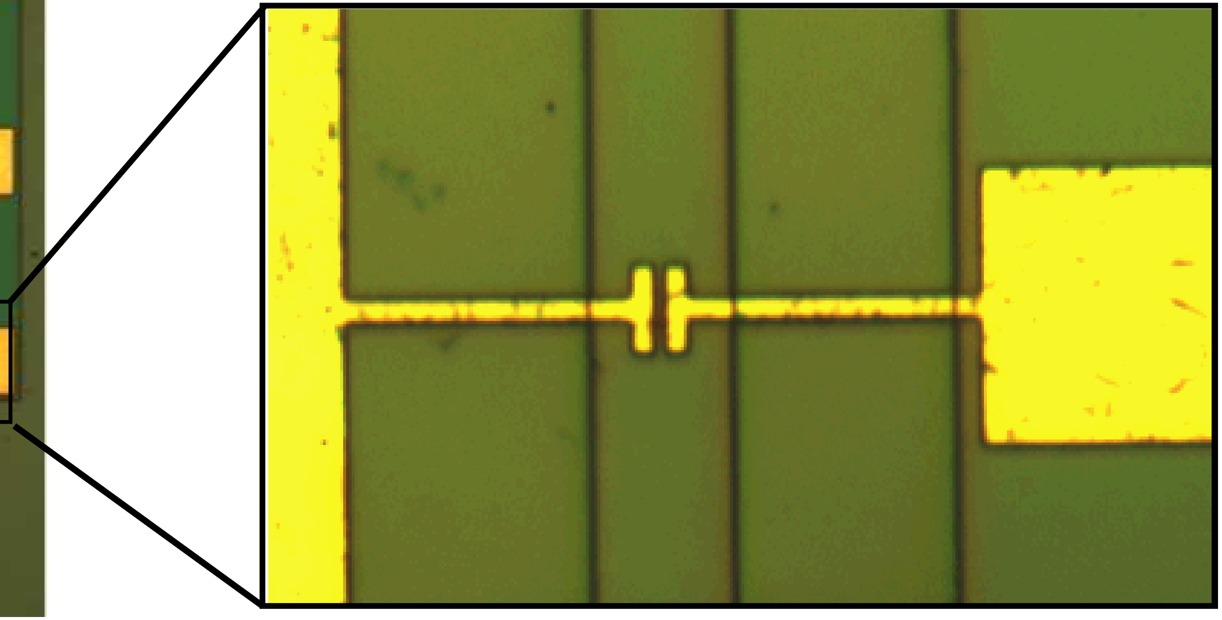
# Validation of Chemical Methods



# Platform Design



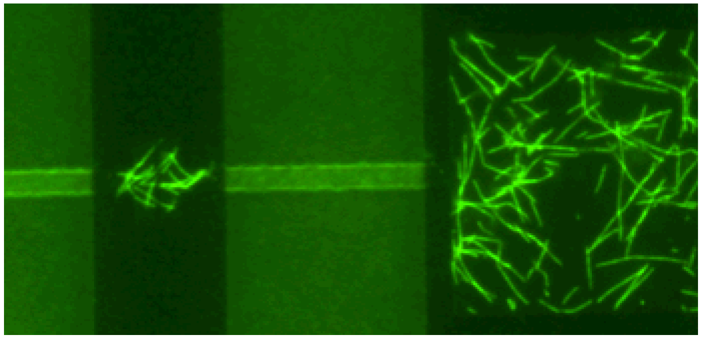

New platform design allows for limited exposure of gold surfaces, localize MT templating

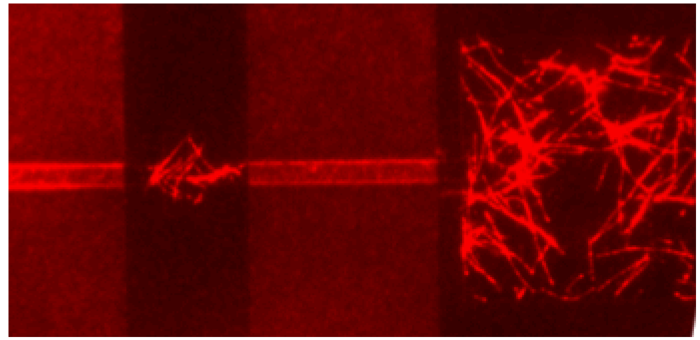


# Assembly "Thermo-dynamics"

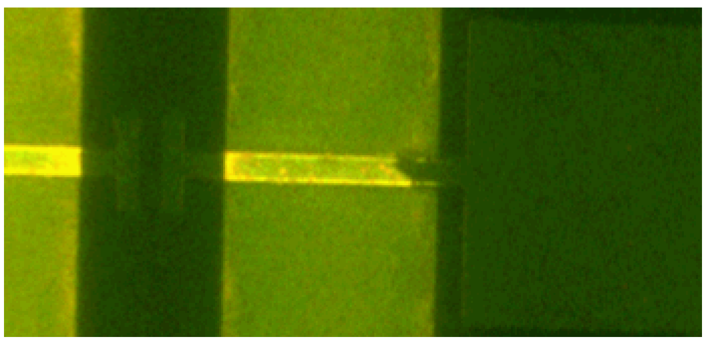
Fluorescent MTs

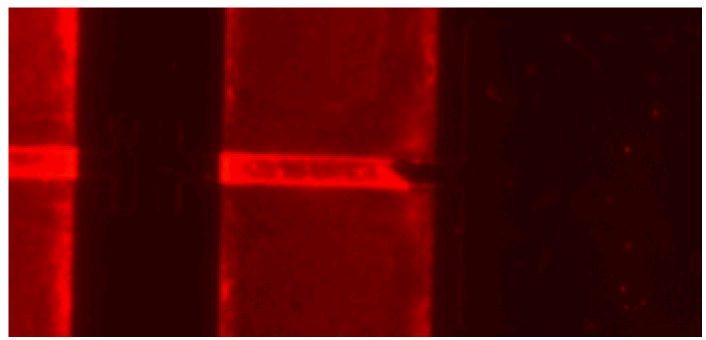
Fluorescent SWNTs on MTs





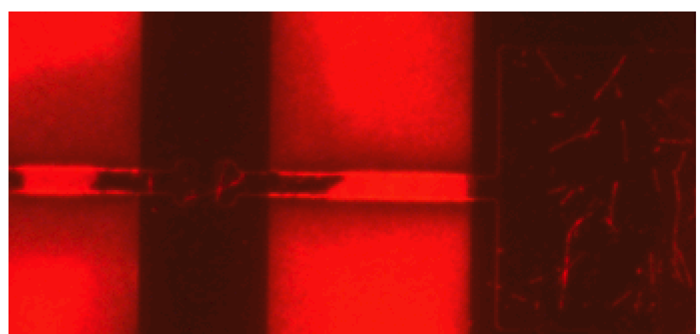
As assembled





After 4°C treatment

Thermal disassembly imitates the dynamic function of MTs in Nature, introducing dynamic character to this assembly.



After reassembly