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"Microtubule Geology" - Applying Microtubules as Biotemplates for Hybrid Nanostructure Growth

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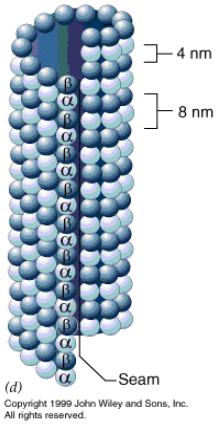
Microtubules: Biological Templates



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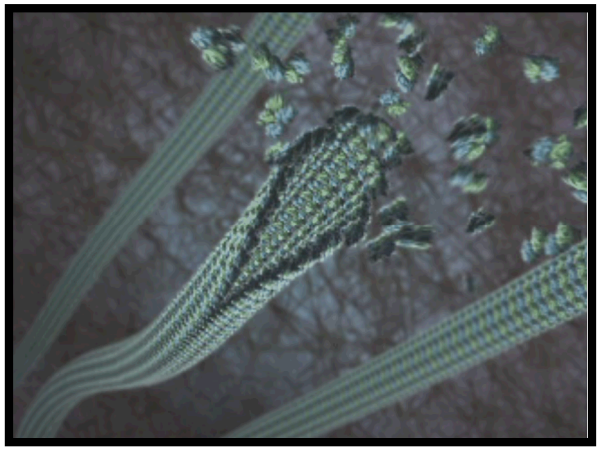
Polar protein filaments (~25 nm diameter)

Polymerized from α-tubulin/β-tubulin dimers

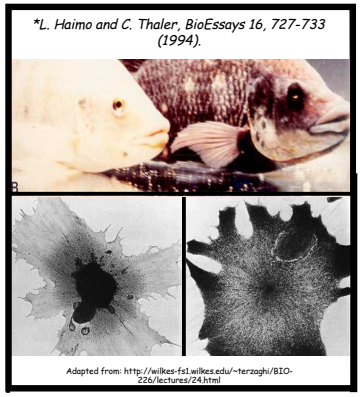
Highly specific interactions with motor proteins (kinesins and dyneins)



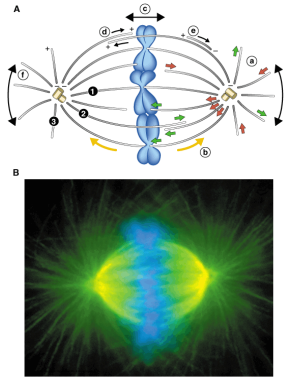
"Inner Life of the Cell," Harvard University

Microtubules (MTs) facilitate a remarkable number of extremely diverse functions throughout biology…

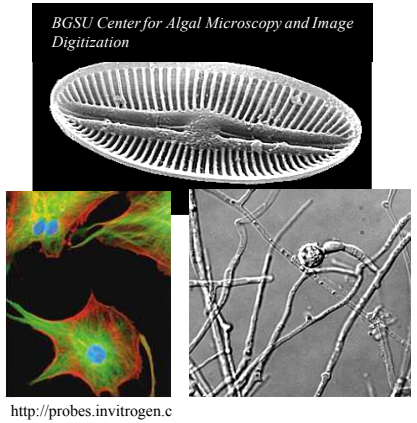
Can we exploit MTs as protein nanowire templates for biomineralization?



Adaptive reorganization of pigment granules in melanophore cells



Chromosome positioning and separation during cell splitting



http://probes.invitrogen.com/

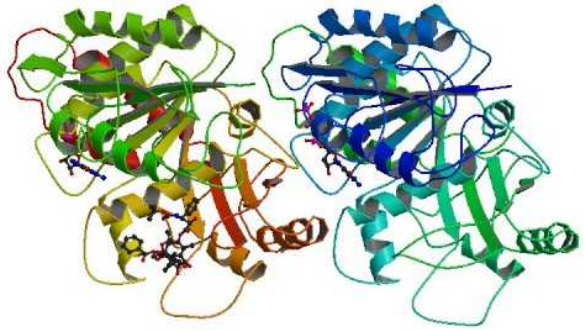
Trafficking of vesicles and macromolecule building blocks

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



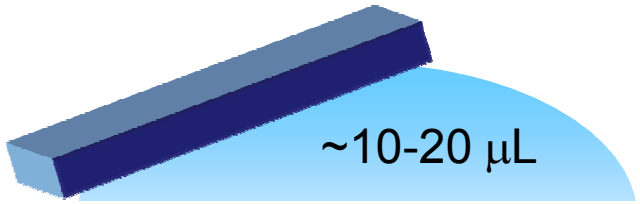
- They exhibit monodispersity in diameter around 25 nm.

- They can be assembled and organized on the nanoscale.

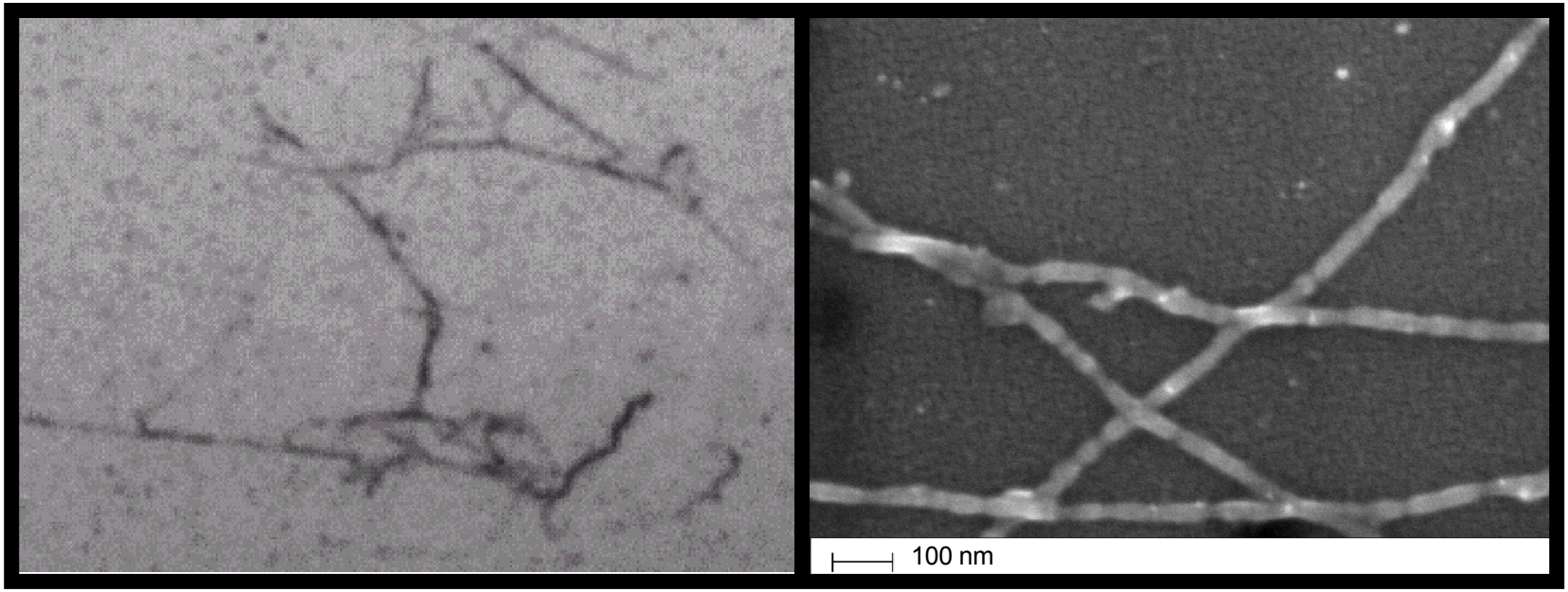
- MT chemistry and assembly can be manipulated for complex templating.

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.

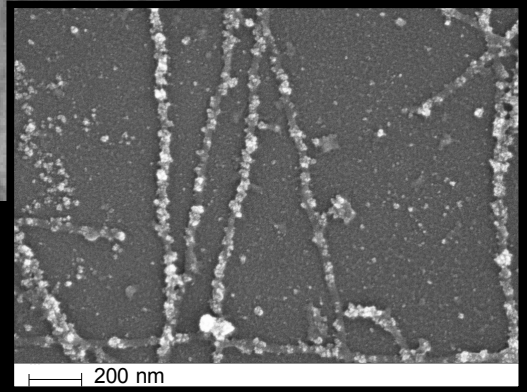


Metallization of microtubules with silver (Ag)

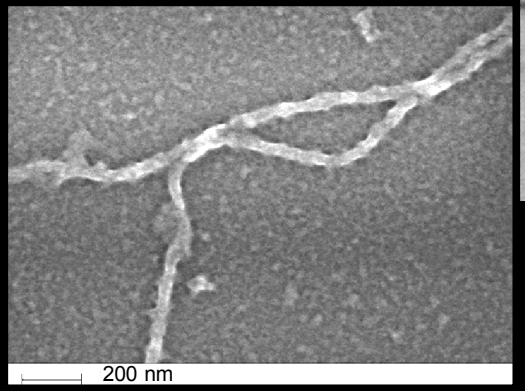


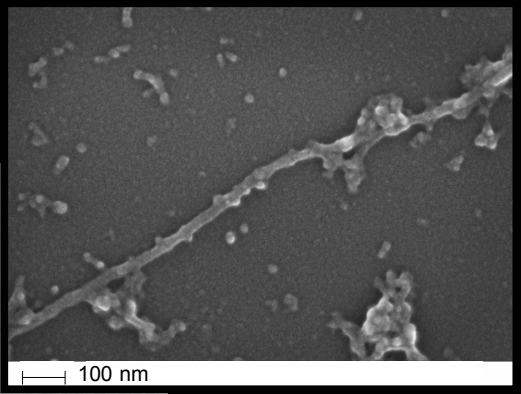
Metallization Diversity

Fe

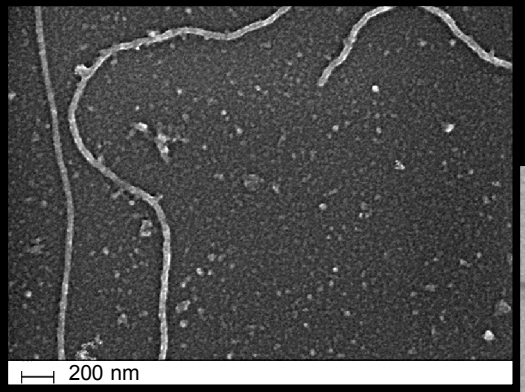


Co





Cu



Mn

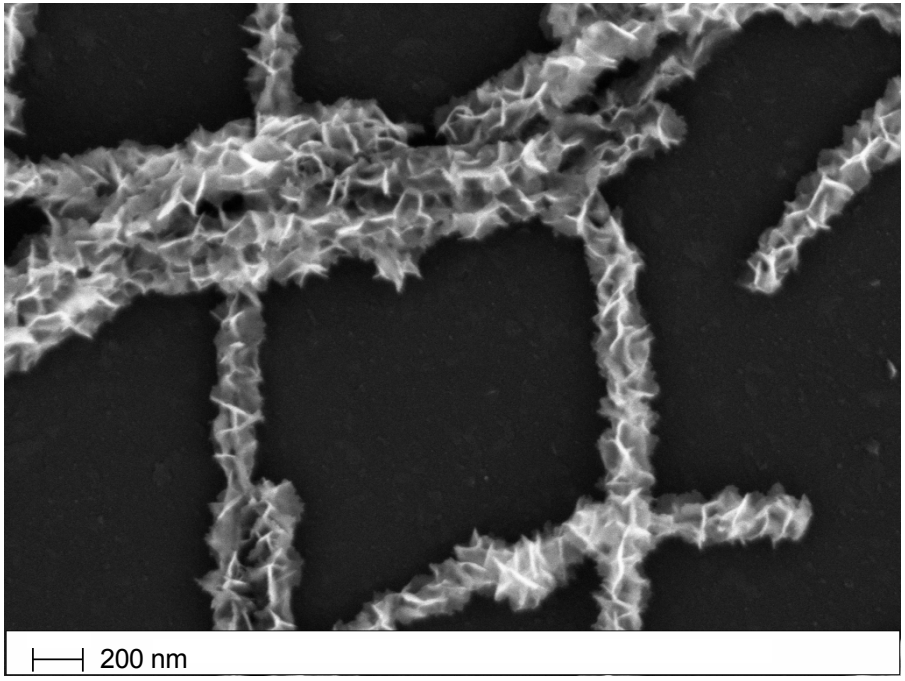
Microtubule Mineralization

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

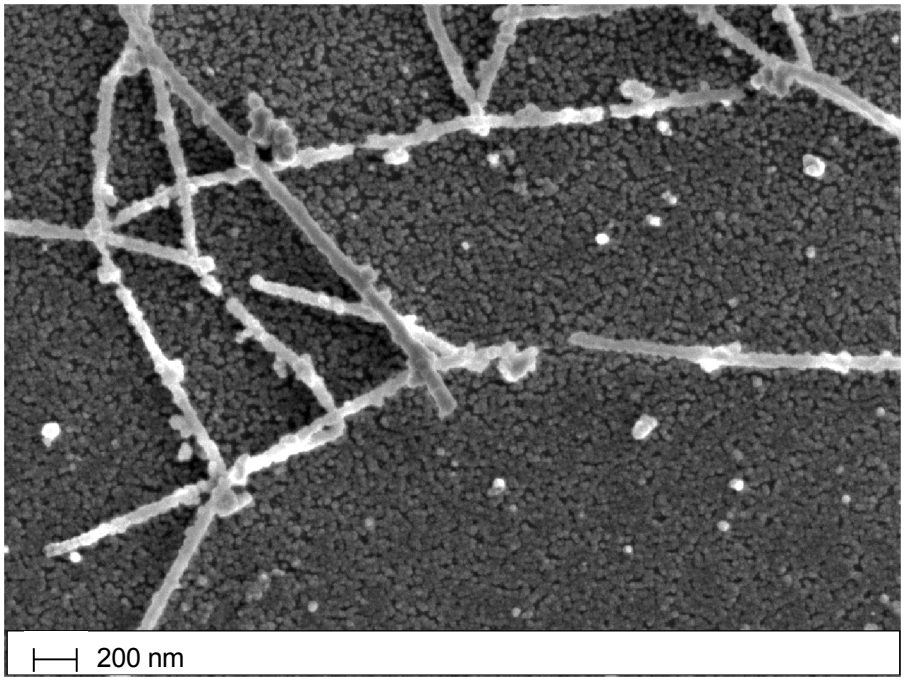
$$4Fe(OH)_2 + 4OH^- + O_2 \longrightarrow 4FeOOH + H_2O + 2O^{2-}$$



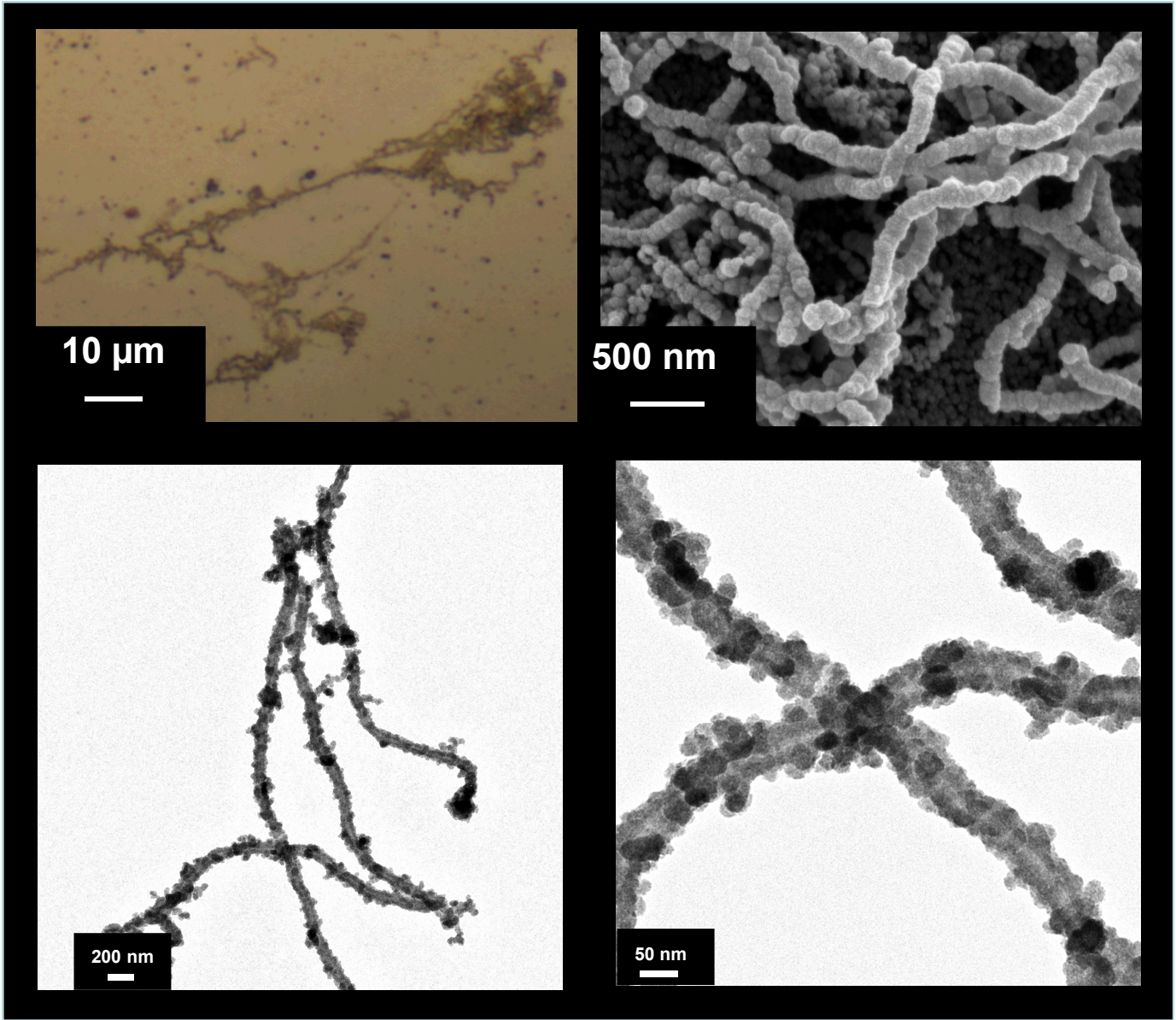
Cadmium sulfide

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

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



A Closer Look at MT-Templated CdS

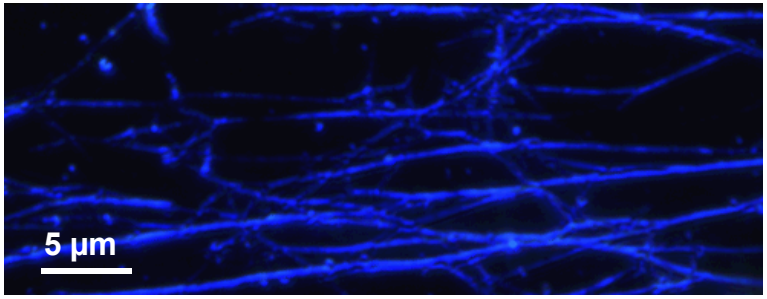


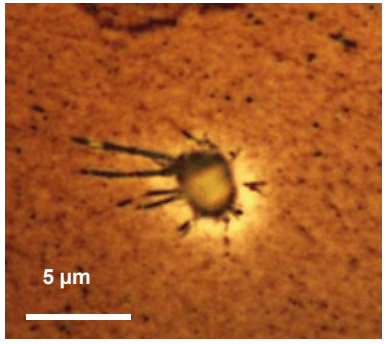
MT surface chemistry promotes dense, conformal CdS mineralization.

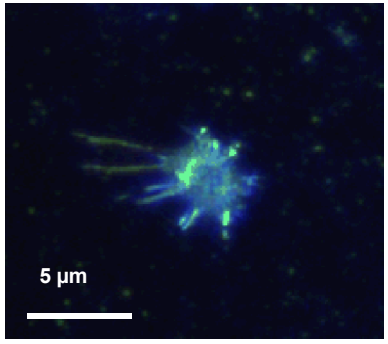
Mineralization is limited to the “bulk” of the protein assemblies – the central pore of the MT is preserved during CdS growth.

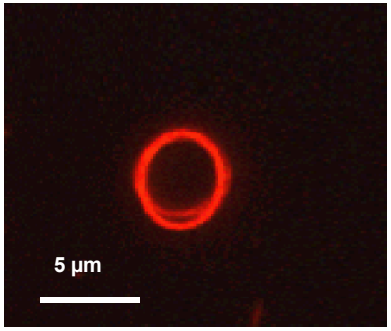
Templating Bio-Mediated Morphologies

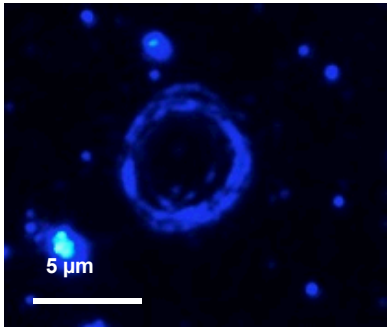
The biological character of MTs allows us to template the growth of unique, non-equilibrium CdS nanostructures

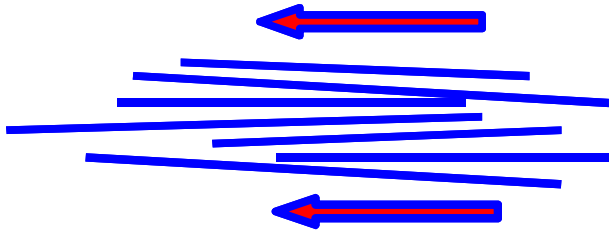


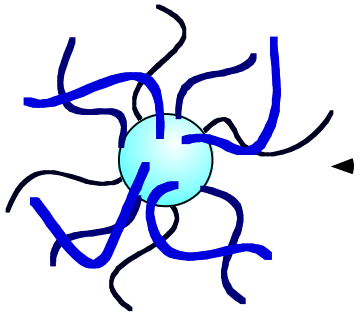


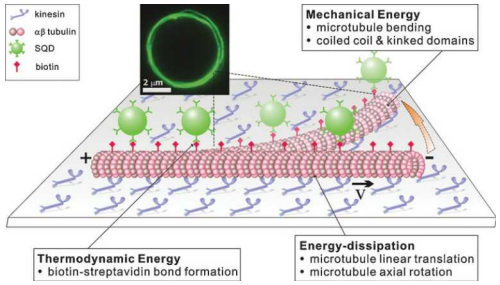






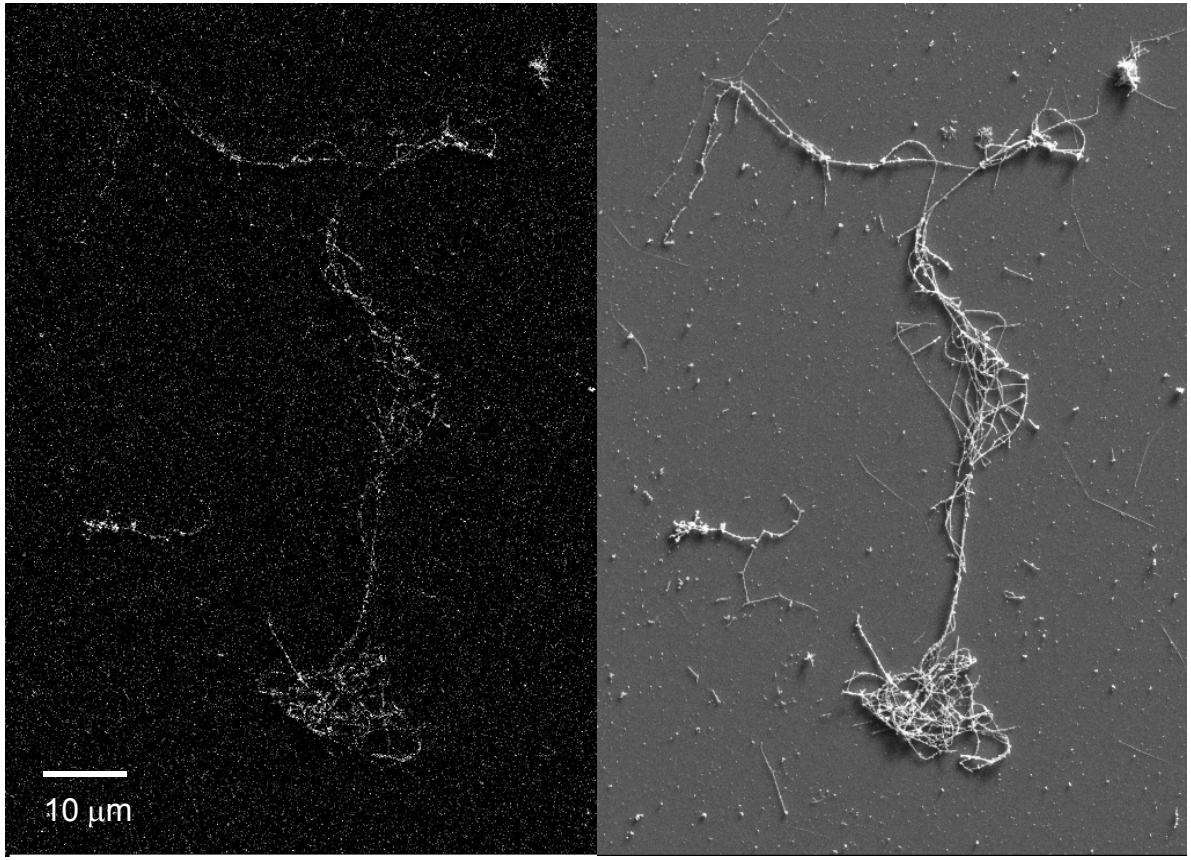






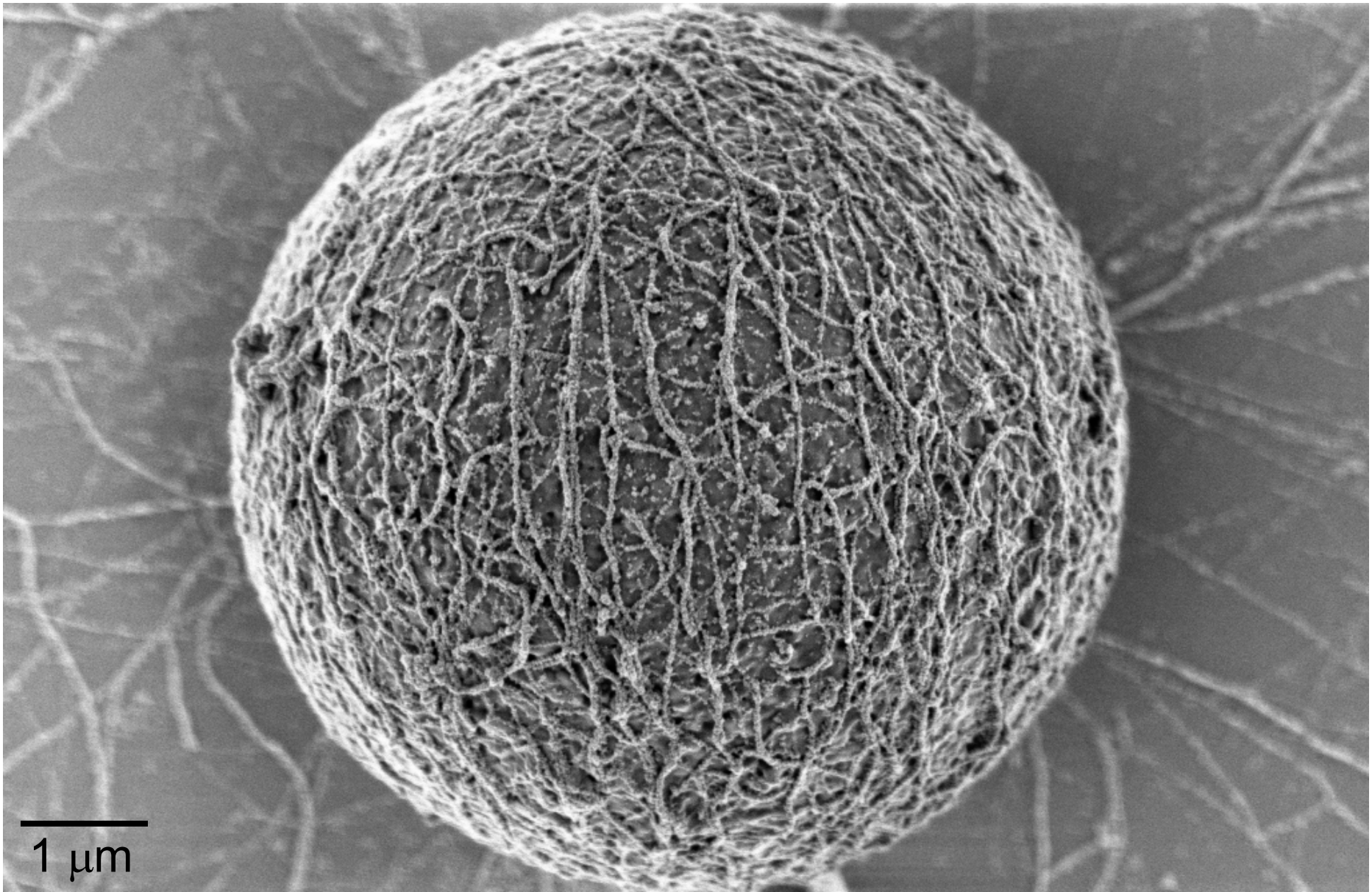
Templating Luminescent Nanostructures

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



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

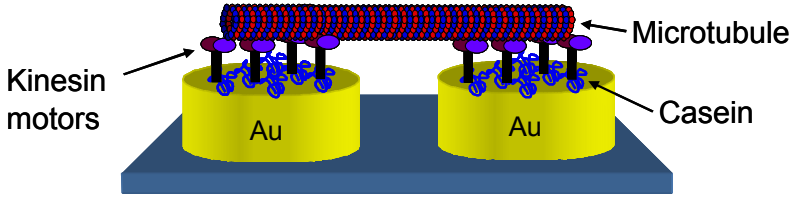
Metallized Architectures

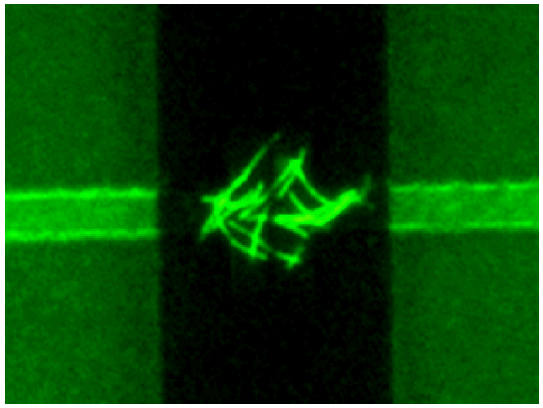


Applying Biometallization

Motor proteins can be selectively bound to gold surfaces and used to capture MT bridges between gold electrodes.

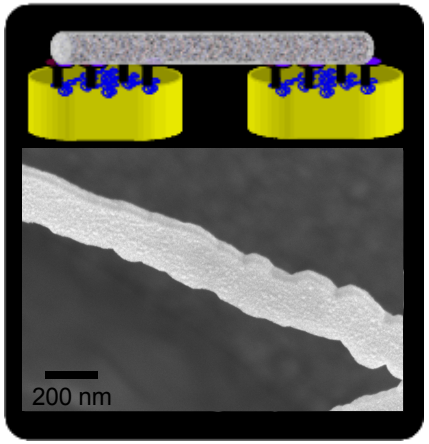
Metallization or mineralization of these bridges forms engineered nanointerconnects.





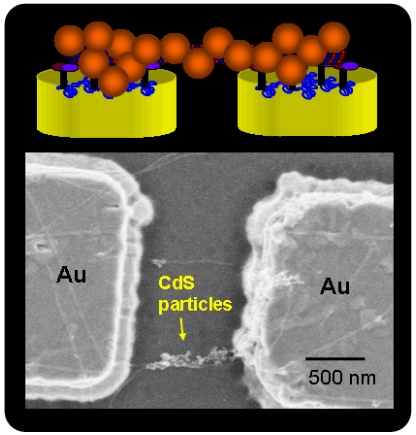
Ag metallization

electrical interconnects (<100Ω)



CdS mineralization

metal/semiconductor junctions



Templating Mixed Materials

Au/Ag

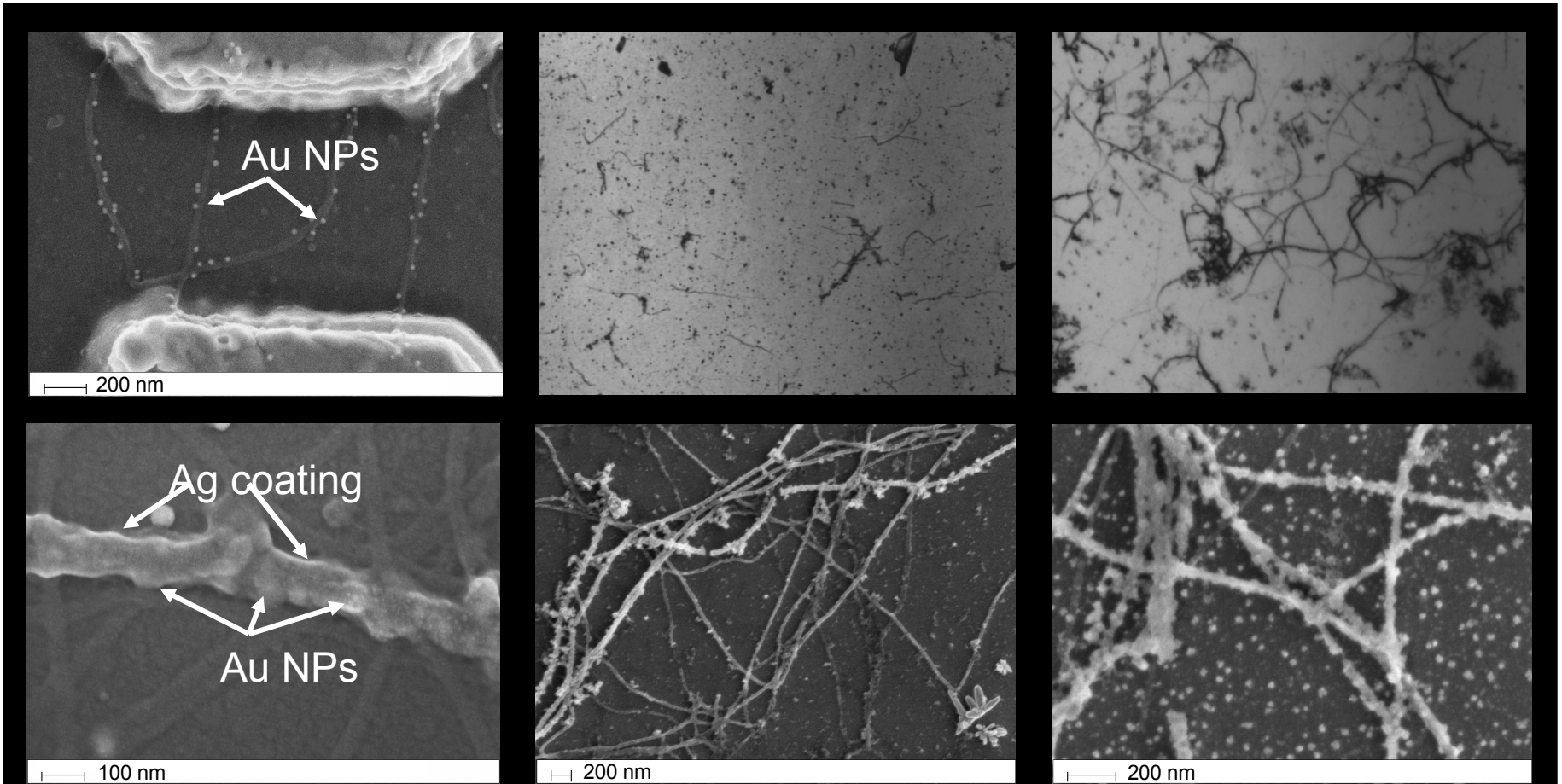
1. Treat biotinylated MTs with anti-biotin Au
2. Incubate with Ag^+
3. Reduce with hydroquinone

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

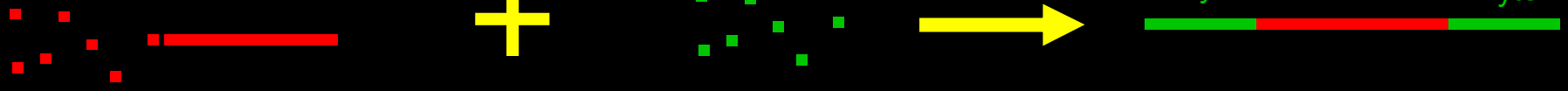


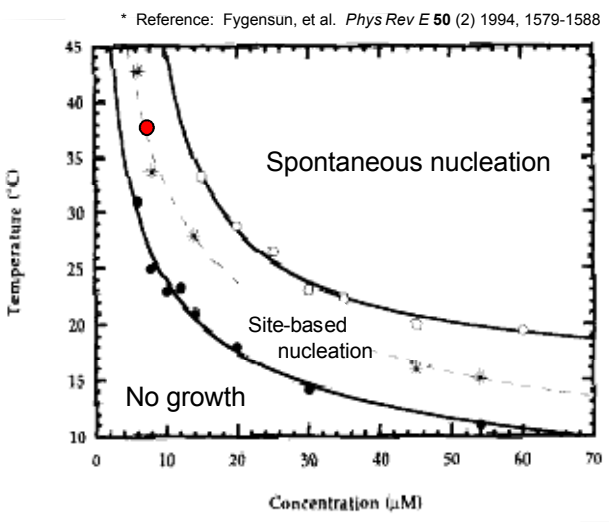
Multifunctional Templates

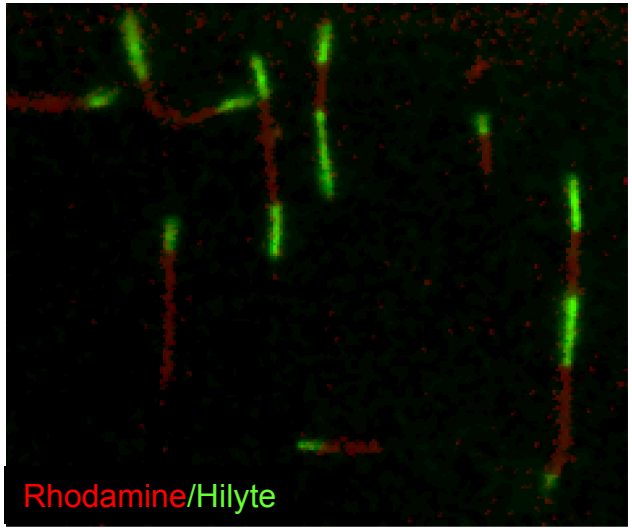
Controlling MT polymerization allows the formation of functionally segmented MTs

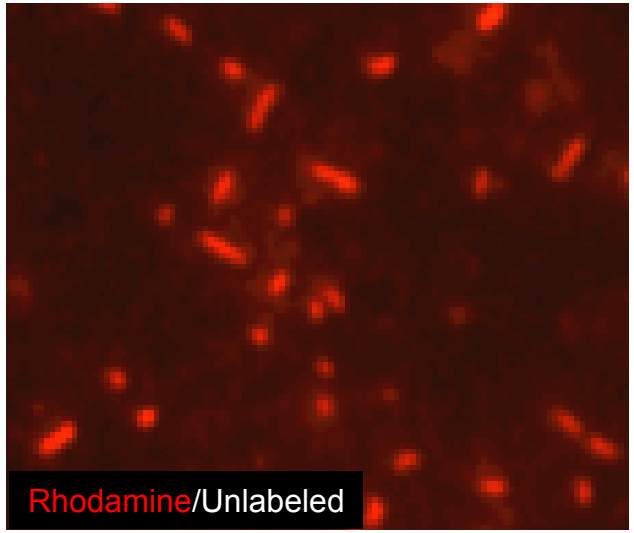
1. Grow rhodamine labeled microtubule 20 min, 37°C

2. Add diluted Hilyte-488 labeled tubulin 20 min 37°C



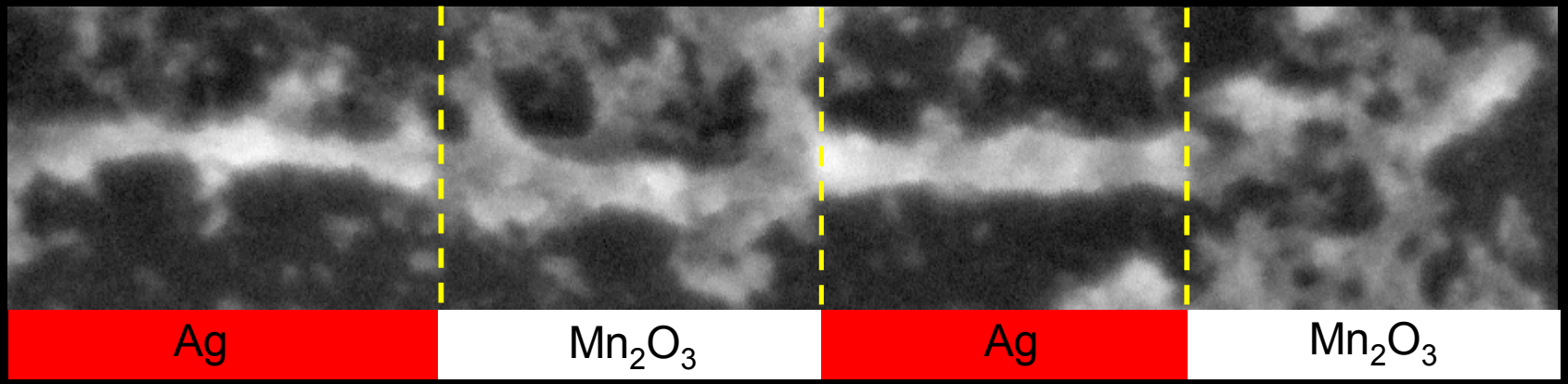


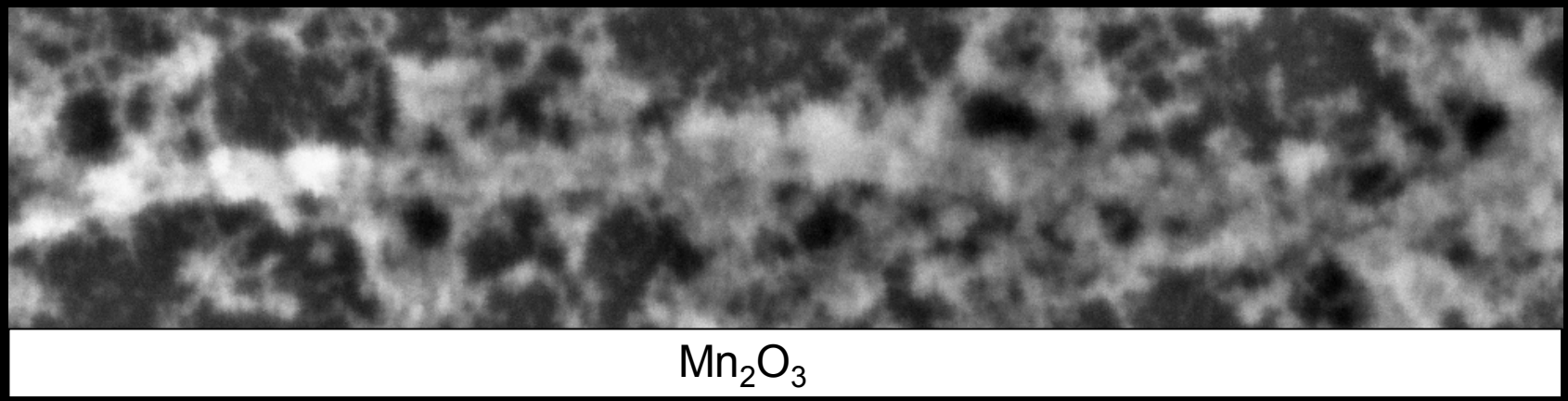




Nanoengineered Hybrid Templates

Functionally segmented MTs produce nanoscale spatially-resolved, selective mineralization





Summary and Conclusions

✓ MTs are versatile biological nanowires in Nature.

✓ Taking advantage of their diverse biofunctional character we can use these structures to template a wide range of metals, oxides, sulfides, and hybrid materials.

✓ Microtubule templates can be integrated and assembled to form complex, bio-enabled architectures.

✓ Manipulating the polymerization and multifunctional character of microtubules, we can create unique, spatially-resolved hybrid nanowires.

Take home message:

Creative uses of biological tools can facilitate the development of new strategies for nanomaterials synthesis and assembly

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