Bio-Inspired Growth of Cadmium Sulfide Nanotubes on Microtubule Templates

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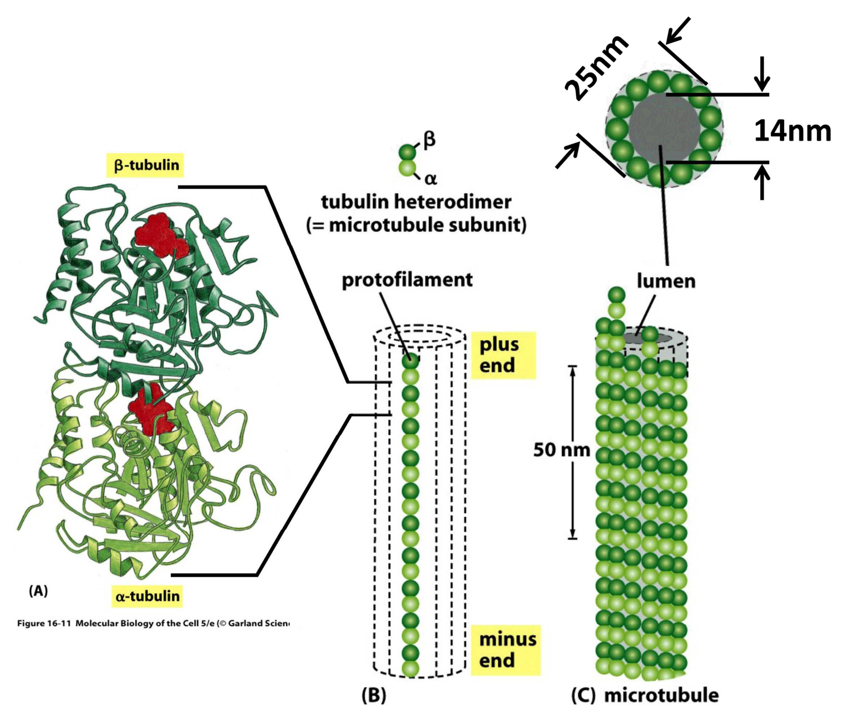
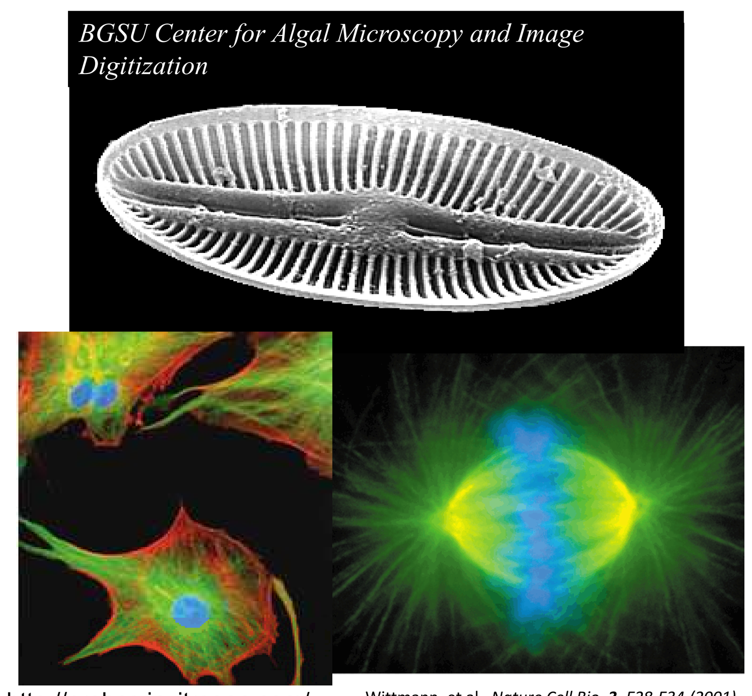
Background

Microtubules (MTs):

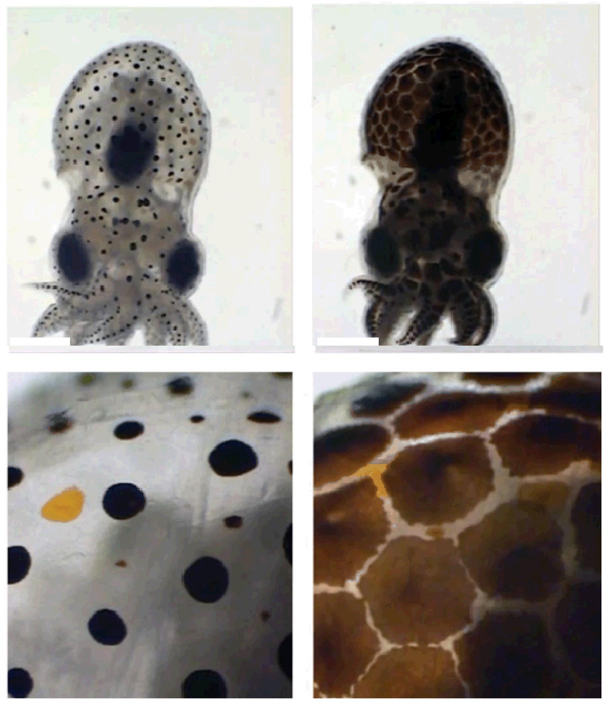
Protein nanotubes polymerized from α-tubulin/β-tubulin heterodimers.

Uniformly ~25 nm diameter, ~14 nm lumen, micrometers in length.





http://probes.invitrogen.com/ Wittmann, et al. *Nature Cell Bio.* **3**, E28-E34 (2001)

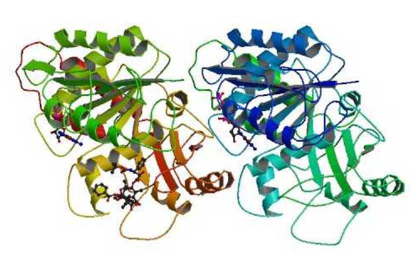


E. Kreit, et al. *Journal of the Royal Society, Interface / the Royal Society* (2012)

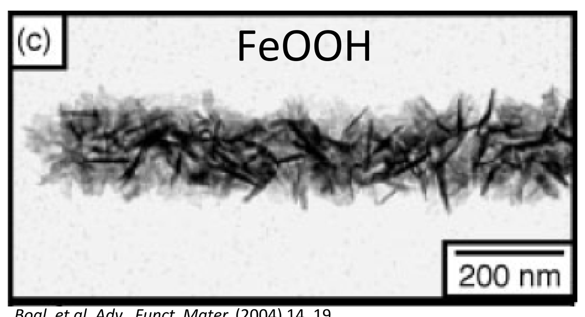
MTs interact with a variety of Microtubule Associated Proteins (MAPs) to direct assembly into functional, secondary assemblies.

- Structural MAPs (e.g., Tau, MAP II)
- Dynamic MAPs (e.g., kinesin)

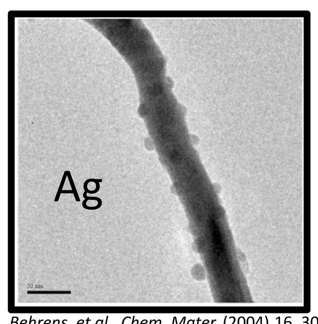
Rich MT protein chemistry also makes these uniform nanofibers attractive as biomineral templates.



- Positive charges: Lysines, Arginines
- Negative charges: Glutamic acid, aspartic acid
- Chelators: Histidine
- Thiol chemistry: Cysteines



Bool, et al. *Adv., Funct. Mater.* (2004) 14, 19



Behrens, et al., *Chem. Mater.* (2004) 16, 3085

Challenges:

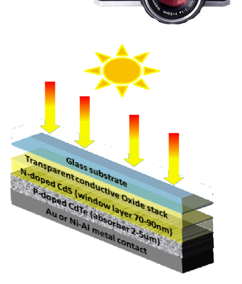
1. *Can MTs be used to template a semiconductor like Cadmium Sulfide (CdS)?*
2. *Can these MT templates be used to create secondary CdS nanostructures?*

Experimental Approach

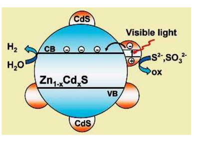
Materials Selection: Cadmium Sulfide

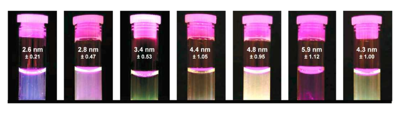
n-type semiconductor (Eg = 2.4-2.5 eV)

Crystallographic polymorphs
- Hexagonal (a = 0.413 nm, c = 0.671 nm)
- Cubic (a = 0.583 nm)



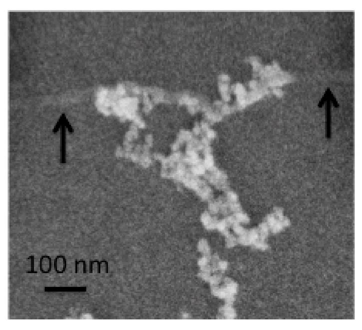
Applications
- Fluorescent probes
- Photoresistors
- Pigments
- Photocatalysts
- Photovoltacis





Limitations of "simple" chemical processing

1. Polymerize MTs in polymerization buffer at 37°C.
2. Incubate polymerized MTs in aqueous Cd^{2+}.
3. Add sodium sulfide (Na_2S).



Rapid reaction of free S^{2-} with Cd^{2+} produces non-uniform CdS growth and poor templating!

Consider a bio-inspired mineralization strategy

Controlled reagent release from organic precursor.

1. Polymerize MTs in polymerization buffer at 37°C.
2. Incubate MTs in aqueous Cd^{2+} and thioacetamide.
3. Raise pH through NH_4OH vapor diffusion

Initiates $Cd(OH)_2$-mediated S^{2-} release from thioacetamide

$$CH_3C(S)NH_2 + H_2O \xrightleftharpoons{Cd(OH)_2} CH_3C(O)NH_2 + H_2S\ (HS^- + H^+)$$

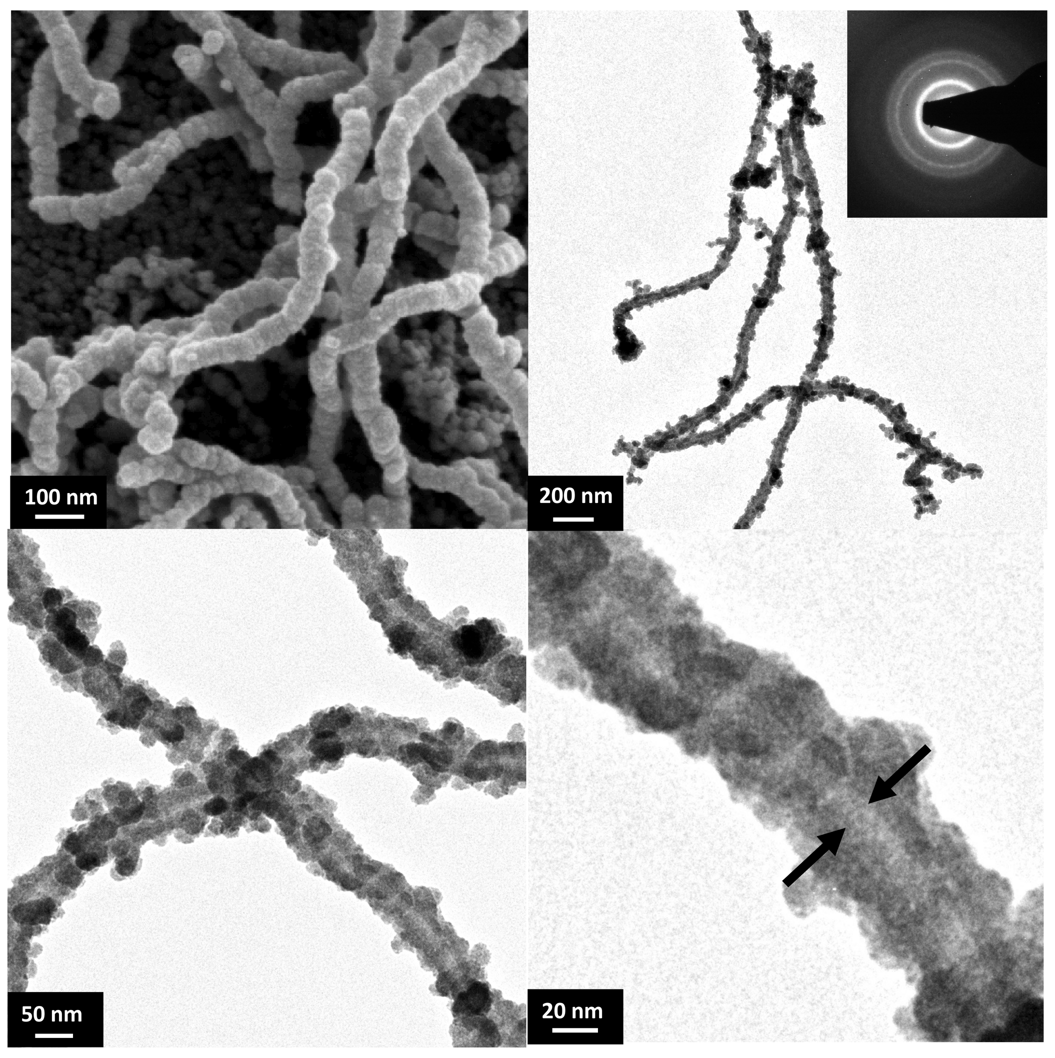
Drives uniform CdS mineralization

$$Cd^{2+} + HS^- \longrightarrow CdS(s) + H^+$$

Spoerke, E., *et al. J. Phys. Chem. C* **2009**, 113, 16329-16336.

Templating CdS

CdS Nanotube Formation

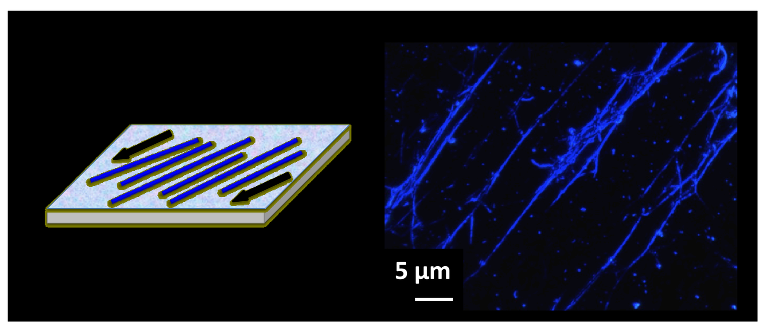


CdS forms a dense, uniform nanocrystalline coating of cubic CdS along MT templates.

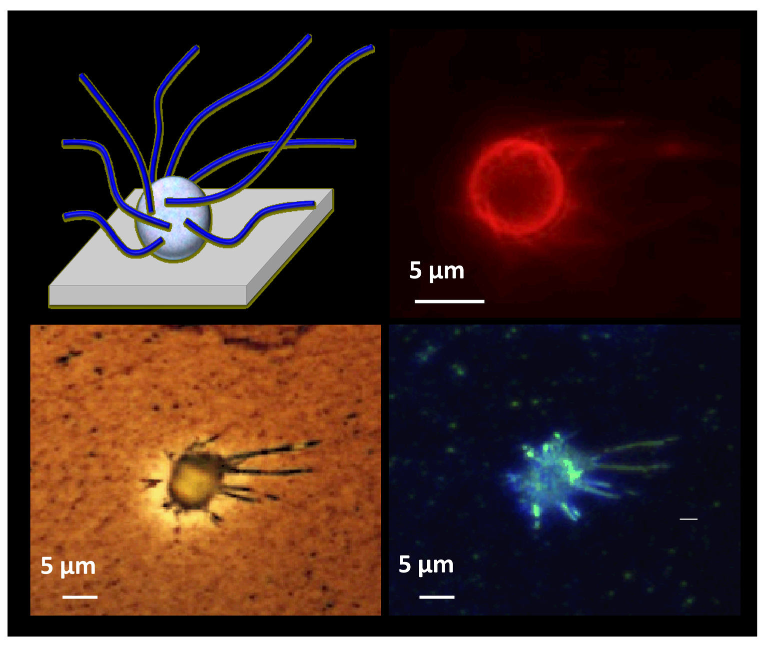
CdS replicates tubular morphology of MTs, forming a CdS nanotube only 1-2 nanocrystals thick!

Secondary Assemblies

When templated onto preformed MT assemblies, CdS forms unique, three-dimensional nanotube architectures and assemblies.



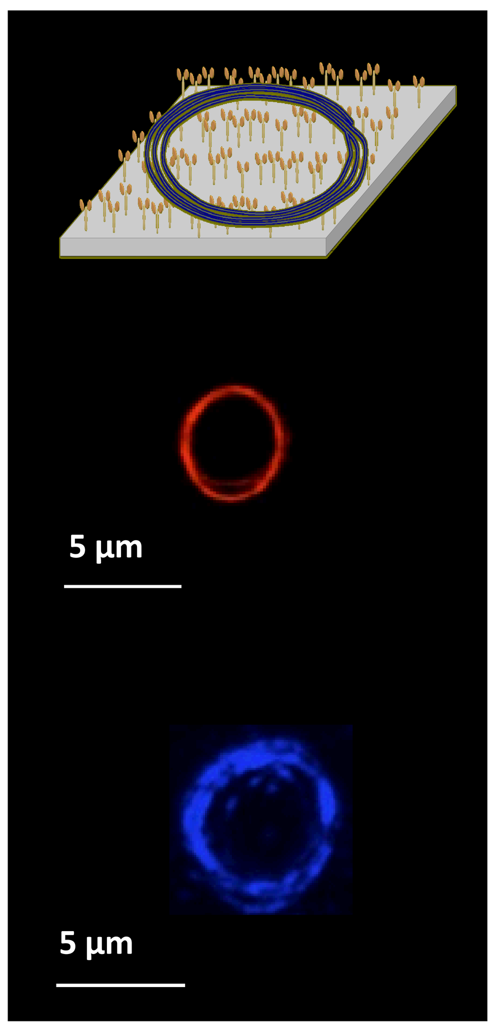
Map II and Tau protein capture MTs flowing over a surface. Resulting MT arrays template aligned CdS nanotubes (seen as blue in dark field).



Map II and Tau protein organize MT growth/assembly into 3D MT asters. (Red Fluorescent)

Templating on these structures creates 3D CdS nanotube asters visible in the brightfield (left) and darkfield (right) images.

Spoerke, et al." *ACS Nano*, DOI: 10.1021/nn303998k, (2012).



ATP-fueled kinesin motor proteins, bound to a surface, drive biotinylated MT assembly into rings (red fluorescent) in the presence of streptavidin.

Templating onto these structures creates nanotuble rings of CdS, (blue in the dark field image).

Liu, *et al. Advanced Materials.* **20** (23), 4476-4481 (2008).

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